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The Environmental Survey Manual

Appendix D

August 1987

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APPENDIX D

ANALYTICAL METHODS

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CONTENTS

Page

ORGANIC ANALYSIS METHODS D-1

VOLATILE ORGANIC COMPOUNDS D-2

  Hexadecane Extraction of Volatiles from Water and Soil/Sediment for Optional Screening D-6
  Optional Screening of Hexadecane Extracts for Volatiles D-11
  GC/MS Analysis of Volatiles D-16

SEMIVOLATILE ORGANIC COMPOUNDS D-80

  Sample Preparation for Semivolatiles in Water D-84
  Medium Level Preparation for Screening and Analysis of Semivolatiles in Soil/Sediment D-93
  Low Level Preparation for Screening and Analysis of Semivolatiles in Soil/Sediment D-99
  Screening of Semivolatile Organic Extracts D-113
  GC/MS Analysis of Semivolatiles D-118

PESTICIDES/PCBS D-170

  Sample Preparation for Pesticides/PCBs in Water D-173
  Medium Level Preparation for Analysis of Pesticides/PCBs in Soil/Sediment D-184
  Low Level Preparation for Analysis of Pesticides/PCBs in Soil/Sediment D-193
  GC/EC Analysis of Pesticides/PCBs D-209

INORGANIC ANALYSIS METHODS D-265

  Determination of Metals by Inductively Coupled Plasma-Atomic Emission Spectrometry D-266
  Determination of Individual Metals by Furnace Atomic Absorption Spectrophotometry D-314
  Mercury in Water by Manual Cold Vapor AA D-363
  Mercury in Sediments by Manual Cold Vapor AA D-381
  Analysis of Hexavalent Chromium by Atomic Absorption Spectrophotometry D-398

NON-TARGET LIST PARAMETERS D-402

OTHER ORGANICS D-403

  Oil and Grease D-404
  Total Organic Carbon D-409

CONTENTS (Continued)

Page

OTHER INORGANICS D-414

Total Cyanide D-415
Hydrogen Cyanide and Hydrogen Sulfide D-427
Chlorine, Total Residual D-434
Residue, Filterable D-439
Residue, Non-filterable D-443

ANIONS D-448

Determination of Inorganic Anions in Aqueous and Solid Samples by Ion Chromatography D-449

HAZARDOUS WASTE CHARACTERISTICS D-474

Corrosivity Characteristic D-475
Ignitability Characteristic D-478
Reactivity Characteristic D-481

TOXICITY CHARACTERISTIC LEACHING PROCEDURE D-490

RADIOLOGICAL .... D-

Determination of Alpha and Beta (Gross Activity) in Water D-508
Determination of Alpha and Beta (Gross Activity) in Air Filters D-512
Gamma Spectroscopy D-518
Isotopic Composition of Uranium or Plutonium D-525
Determination of Plutonium Isotopes in Water D-553
Determination of Plutonium Isotopes in Air Filters D-561
Determination of Plutonium in Water D-570
Determination of Plutonium in Sediment and Soil D-578
Determination of Uranium Isotopes in Water D-587
Determination of Uranium Isotopes in Sediment and Soil D-594
Determination of Uranium Isotopes in Air Filters D-602
Determination of Uranium (Total) in Water by Fluorometric Analysis .. D-610
Determination of Uranium in Water D-616
Determination of Uranium in Soils, Sediments, and Sludges D-626
Determination of Thorium (Alpha-Emitting) Isotopes in Water D-637
Determination of Thorium (Alpha-Emitting) Isotopes in Sediment and Soil D-645
Determination of Thorium (Alpha-Emitting) Isotopes in Air Filters ... D-656
Determination of Thorium in Water D-667
Determination of Thorium in Sediment and Soil D-673
Determination of Strontium-90 in Water D-679
Determination of Strontium-90 in Sediment and Soil D-687
Determination of Iodine-131 in Air Filters D-697
Determination of Technetium-99 in Water D-7
Determination of Technetium-99 in Sediment and Soil D-7
Determination of Technetium-99 in Air Filters D-711
Americium-241 and Curium-244 in Water, Radiochemical Method D-715
Gamma-Ray Emitting Nuclides in Water D-722

ORGANIC
ANALYSIS METHODS

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VOLATILE ORGANIC COMPOUNDS

The following methods address the determination of the volatile (purgeable) organic compounds listed in Table D-1. The methods include hexadecane extraction, screening, and analysis. The hexadecane extraction and screening are optional methods conducted to determine approximate concentrations of volatiles in the sample. These methods are included to aid the analyst in determining conditions for analysis. The analytical method is based on EPA Method 624.

Table D-1. Analytes Determined by CLP Volatiles Analysis Method

		Contract Required Detection Limits[a]	
Analyte	CAS Number	Water (ug/L)	Low Soil/Sediment[b, c] (ug/kg)
1. Chloromethane	74-87-3	10	10
2. Bromomethane	74-83-9	10	10
3. Vinyl chloride	75-01-4	10	10
4. Chloroethane	75-00-3	10	10
5. Methylene chloride	75-09-2	5	5
6. Acetone	67-64-1	10	10
7. Carbon disulfide	75-15-0	5	5
8. 1,1-Dichloroethene	75-35-4	5	5
9. 1,1-Dichloroethane	75-35-3	5	5
10. 1,2-Dichloroethene (total)	540-59-0	5	5
11. Chloroform	67-66-3	5	5
12. 1,2-Dichloroethane	107-06-2	5	5
13. 2-Butanone	78-93-3	10	10
14. 1,1,1-Trichloroethane	71-55-6	5	5
15. Carbon tetrachloride	56-23-5	5	5
16. Vinyl acetate	108-05-4	10	10
17. Bromodichloromethane	75-27-4	5	5
18. 1,1,2,2-Tetrachloroethane	79-34-5	5	5
19. 1,2-Dichloropropane	78-87-5	5	5
20. cis-1,3-Dichloropropene	10061-01-5	5	5
21. Trichloroethene	79-01-6	5	5
22. Dibromochloromethane	124-48-1	5	5
23. 1,1,2-Trichloroethane	79-00-5	5	5
24. Benzene	71-43-2	5	5
25. trans-1,3-Dichloropropene	10061-02-6	5	5
26. Bromoform	75-25-2	5	5
27. 2-Hexanone	591-78-6	10	10
28. 4-Methyl-2-pentanone	108-10-1	10	10
29. Tetrachloroethene	127-18-4	5	5
30. Toluene	108-88-3	5	5
31. Chlorobenzene	108-90-7	5	5
32. Ethyl benzene	100-41-4	5	5
33. Styrene	100-42-5	5	5
34. Xylenes (total)	133-02-7	5	5

a. Specific detection limits are highly matrix dependent. The detection limits listed herein are provided for guidance and may not always be achievable.

Table D-1. Analytes Determined by CLP Volatiles Analysis Method (Continued)

b. Detection limits listed for soil/sediment are based on wet weight. The detection limits calculated by the laboratory for soil/sediment, calculated on dry weight basis as required by the contract, will be higher.

c. Contract required detection limits (CRDL) for volatiles at medium levels in soil/sediment are 100 times the listed CRDL for volatiles at low levels in soil/sediment.

HEXADECANE EXTRACTION OF VOLATILES FROM WATER AND SOIL/SEDIMENT FOR OPTIONAL SCREENING

1.0 SUMMARY OF METHOD

1.1 For water samples, a 40-mL aliquot of sample is extracted with 2 mL of hexadecane. This provides a minimum quantitation limit (MQL) of:

Compounds	MQL (ug/L)
Non-halogenated aromatics	40 to 50
Halogenated methanes	800 to 1000
Halogenated ethanes	400 to 500

For soil or sediment samples, 40 mL of reagent water are added to 10 g (wet weight) of soil and shaken. The water phase is in turn extracted with 2 mL of hexadecane. This provides a minimum quantitation limit approximately four times higher than those listed for water.

1.2 The hexadecane extraction and screening protocols for volatiles are optional. These protocols are included to aid the analyst in deciding whether a sample contains low or medium levels of volatiles. The use of these or other screening protocols could prevent saturation of the purge and trap system and/or the GC/MS system. It is recommended that these or other screening protocols be used, particularly if there is some doubt about the level of organics in a sample. This is especially true in soil/sediment analysis.

1.3 These extraction and preparation procedures were developed for rapid screening of water samples from hazardous waste sites. The design of the methods thus does not stress efficient recoveries or low limits of quantitation. Rather, the procedures were designed to screen at moderate recovery and sufficient sensitivity for a broad spectrum of organic chemicals. The results of the analyses thus may reflect only a minimum of the amount actually present in some samples. This is especially true if water soluble solvents are present.

2.0 INTERFERENCES

2.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the total ion current profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks. Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the site being sampled.

3.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

3.1 Samples must be protected from light and refrigerated at 4°C (±2°C) from the time of receipt until analysis or extraction.

3.2 Analysis of water or soil/sediment samples for volatiles must be completed within 10 days of verified time of sample receipt (VTSR).

4.0 APPARATUS AND MATERIALS

4.1 Vials and caps - 2 mL for GC autosampler.

4.2 Volumetric flask - 50 mL with ground-glass stopper.

4.3 Pasteur pipets - Disposable.

4.4 Centrifuge tube - 50 mL with ground-glass stopper or Teflon-lined screw cap.

4.5 Balance - Analytical, capable of accurately weighing ±0.0001 g.

5.0 REAGENTS

5.1 Hexadecane and methanol - Pesticide residue analysis grade or equivalent.

5.2 Reagent water - Reagent water is defined as water in which an interferent is not observed at the CRDL of each analyte of interest.

5.3 Standard Mixture 1 containing benzene, toluene, ethyl benzene, and xylene. Standard Mixture 2 containing n-nonane and n-dodecane.

5.3.1 Stock standard solutions (1.00 ug/uL) - Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

5.3.1.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in methanol and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. If compound purity is certified at 96 percent or greater, the weight can be used without correction to calculate the concentration of the stock standard.

5.3.1.2 Transfer the stock standard solutions into multiple Teflon-sealed, screw-cap vials. Store, with no headspace, at -10°C to -20°C, and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. These solutions must be replaced after six months, or sooner if comparison with quality control check samples indicates a problem. Standards prepared from gases or reactive compounds such as styrene must be replaced after two months, or sooner if comparison with quality control check samples indicates a problem.

5.3.2 Prepare working standards of Standard Mixtures 1 and 2 at 100 ng/uL of each compound in methanol. Store these solutions as in Section 5.3.1.2 above.

6.0 PROCEDURE

6.1 Water Samples

6.1.1 Remove a 40-mL aliquot from the sample and allow the aliquot to come to room temperature. Quickly transfer the 40-mL sample to a 50-mL volumetric flask. Immediately add 2.0 mL of hexadecane, cap the flask, and shake vigorously for 1 min. Let phases separate. Open the flask and add sufficient reagent water to bring the hexadecane layer into the neck of the flask.

6.1.2 Transfer approximately 1 mL of the hexadecane layer to a 2.0-mL GC vial. If an emulsion is present after shaking the sample, break it by:

1. Pulling the emulsion through a small plug of Pyrex glass wool packed in a pipet, or

2. Transferring the emulsion to a centrifuge tube and centrifuging for several minutes.

6.1.3 Add 200 uL of working Standard Mixture 1 and 2 to separate 40-mL portions of reagent water. Follow Sections 6.1.1-6.1.2 beginning with the immediate addition of 2.0 mL of hexadecane.

6.2 Soil/Sediment Samples

6.2.1 Add approximately 10 g of soil (wet weight) to 40 mL of reagent water in a 50-mL centrifuge tube with a ground glass stopper or Teflon-lined cap. Cap and shake vigorously for 1 min. Centrifuge the capped flask briefly. Quickly transfer supernatant water to a 50-mL volumetric flask equipped with a ground-glass stopper.

6.2.2 Follow instructions in Section 6.1, starting with the addition of 2.0 mL of hexadecane.

6.3 Submit extracts for optional screening.

OPTIONAL SCREENING OF HEXADECANE EXTRACTS FOR VOLATILES

1.0 SUMMARY OF METHOD

1.1 The hexadecane extracts of water and soil/sediment are screened on a gas chromatograph/flame ionization detector (GC/FID). The results of the screen will determine if volatile organics are to be analyzed by low or medium level GC/MS procedures if the sample is a soil/sediment, or to determine the appropriate dilution factor if the sample is water.

1.2 The flame ionization detector varies considerably in sensitivity when comparing aromatics and halogenated methanes and ethanes. Halomethanes are approximately 20 times less sensitive than aromatics and haloethanes are approximately 10 times less sensitive. Low molecular weight, water soluble solvents, e.g., alcohols and ketones, will not extract from the water, and therefore will not be detected by the GC/FID.

2.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

2.1 Samples must be protected from light and refrigerated at 4°C (±2°C) from the time of receipt until analysis or extraction.

2.2 Analysis of water or soil/sediment samples for volatiles must be completed within 10 days of verified time of sample receipt (VTSR).

3.0 APPARATUS AND EQUIPMENT

3.1 Gas chromatograph - An analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector, and strip-chart recorder. A data system is recommended for measuring peak areas.

3.1.1 Flame ionization detector.

3.1.2 GC column - 3 m x 2 mm I.D. glass column packed with 10 percent OV-101 on 100-120 mesh Chromosorb W-HP (or equivalent). The column temperature should be programmed from 80°C to 280°C at 16°C/min and held at 280°C for 10 min.

4.0 REAGENTS

4.1 Hexadecane - Pesticide residue analysis grade or equivalent.

5.0 PROCEDURE

5.1 Extract Screening

5.1.1 External standard calibration - Standardize the GC/FID each 12-h shift for half scale response. This is done by injecting 1 to 5 uL of the hexadecane extracts that contain approximately 10 ng/uL of the Standard Mixture 1 and Standard Mixture 2 compounds. Use the GC conditions specified in Section 3.1.2.

5.1.2 Inject the same volume of hexadecane extract as the extracted standard mixture in Section 5.1.1. Use the GC conditions specified in Section 3.1.2.

5.2 Analytical Decision

5.2.1 Following are two options for interpreting the GC/FID chromatogram.

5.2.1.1 Option A is to use Standard Mixture 1 containing the aromatics to calculate an approximate concentration of the aromatics in the sample. Use this information to determine the proper dilution for purge and trap GC/MS analysis if the sample is a water or whether to use the low or medium level purge and trap GC/MS analysis method if the sample is a soil/sediment (see Table 1 for guidance). This should be the best approach, however, the aromatics may be absent or obscured by higher concentrations of other purgeables. In these cases, Option B may be the best approach.

5.2.1.2 Option B is to use Standard Mixture 2 containing n-nonane and n-dodecane to calculate a factor. Use the factor to calculate a dilution for, purge and trap GC/MS analysis of a water sample or to determine whether to use the low or medium level purge and trap GC/MS analysis method for soil/sediment samples (see Table 1 for guidance). All purgeables of interest have retention times less than the n-dodecane.

5.2.2 Water Samples

Compare the chromatograms of the hexadecane extract of the sample with those of the reagent blank and extract of the standard.

5.2.2.1 If no peaks are noted, other than those also in the reagent blank, analyze a 5-mL water sample by purge and trap GC/MS.

5.2.2.2 If peaks are present prior to the n-dodecane and the aromatics are distinguishable, follow Option A (Section 5.2.1.1).

5.2.2.3 If peaks are present prior to the n-dodecane but the aromatics are absent or indistinguishable, use Option B (Section 5.2.1.2) as follows:

If all peaks are ≤3 percent of the n-nonane, analyze a 5-mL water sample by purge and trap GC/MS.

If any peaks are ≥3 percent of the n-nonane, measure the peak height or area of the major peak and calculate the dilution factor as follows:

$$\text{Dilution factor} = \frac{\text{Peak area of sample major peak x 50}}{\text{Peak area of n-nonane}}$$

The water sample will be diluted using the calculated factor just prior to purge and trap GC/MS analysis.

5.2.3 Soil/Sediment Samples

Compare the chromatograms of the hexadecane extract of the sample with those of the reagent blank and extract of the standard.

5.2.3.1 If no peaks are noted, other than those also in the reagent blank, analyze a 5-g sample by low level purge and trap GC/MS.

5.2.3.2 If peaks are present prior to the n-dodecane and the aromatics are distinguishable, follow Option A (Section 5.2.1.1) and the concentration information in Table 1 to determine whether to analyze by low or medium level purge and trap GC/MS.

5.2.3.3 If peaks are present prior to the n-dodecane but the aromatics are absent or indistinguishable, use

Option B and calculate an X factor using the following formula:

$$\text{X Factor} = \frac{\text{Peak area of sample major peak}}{\text{Peak area of n-nonane}}$$

5.3 Using the results of the screening, analyze the samples according to the method "GC/MS Analysis of Volatiles."

Table 1. Determination of Purge and Trap GC/MS Method

X Factor	Analyze by	Approximate Concentration Range[a] (ug/kg)
0-1.0	low level method	0-1,000
>1.0	medium level method	>1,000

a. This concentration range is based on the response of aromatics to GC/FID. When comparing GC/FID responses, the concentration for halomethanes is 20 times higher, and that for haloethanes is 10 times higher.

GC/MS ANALYSIS OF VOLATILES

1.0 SUMMARY OF METHOD

1.1 Water Samples

An inert gas is bubbled through a 5-mL sample contained in a specifically designed purging chamber at ambient temperature. The volatiles are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatiles are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the volatiles onto a gas chromatographic column. The gas chromatograph is temperature programmed to separate the volatiles which are then detected with a mass spectrometer.

An aliquot of the sample is diluted with reagent water when dilution is necessary. A 5-mL aliquot of the dilution is taken for purging.

1.2 Soil/Sediment Samples

1.2.1 Low Level. An inert gas is bubbled through a mixture of a 5-g sample and reagent water contained in a suggested specially designed purging chamber (illustrated in Figure 1) at elevated temperatures. The volatiles are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatiles are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the volatiles onto a gas chromatographic column. The gas chromatograph is temperature programmed to separate the volatiles which are then detected with a mass spectrometer.

1.2.2 Medium Level. A measured amount of soil is extracted with methanol. A portion of the methanol extract is diluted to

5 mL with reagent water. An inert gas is bubbled through this solution in a specifically designed purging chamber at ambient temperature. The volatiles are effectively transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatiles are trapped. After purging is completed, the sorbent column is heated and backflushed with the inert gas to desorb the volatiles onto a gas chromatographic column. The gas chromatograph is temperature programmed to separate the volatiles which are then detected with a mass spectrometer.

2.0 INTERFERENCES

2.1 Impurities in the purge gas, organic compounds out-gassing from the plumbing ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks as described in Section 9.0. Avoid using non-TFE tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device.

2.2 Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and methylene chloride) through the septum seal into the sample during storage and handling. A holding blank prepared from reagent water and carried through the holding period and the analysis protocol serves as a check on such contamination. One holding blank per case will be analyzed. Data must be retained by the laboratory and made available for inspection during on-site evaluations.

2.3 Contamination by carry-over can occur whenever high level and low level samples are sequentially analyzed. To reduce carry-over, the purging device and sampling syringe must be rinsed with reagent water between sample analyses. Whenever an unusually concentrated sample is encountered, follow it by an analysis of reagent water to check for cross contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high purgeable levels, it may be necessary to wash out the purging device with a detergent solution, rinse it with distilled water, and then dry it in a 105°C oven between analyses. The trap and other parts of the system are also subject to contamination; therefore, frequent bake-out and purging of the entire system may be required.

2.4 The laboratory where volatile analysis is performed must be completely free of solvents.

3.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

3.1 Samples must be protected from light and refrigerated at 4°C (±2°C) from the time of receipt until analysis or extraction.

3.2 Analysis of water or soil/sediment samples for volatiles must be completed within 10 days of verified time of sample receipt (VTSR).

4.0 APPARATUS AND MATERIALS

4.1 Micro syringes - 25 uL and larger, 0.006-in. I.D. needle.

4.2 Syringe valve - Two-way, with Luer ends (three each), if applicable to the purging device.

4.3 Syringe - 5 mL, gas tight with shut-off valve.

4.4 Balance - Analytical, capable of accurately weighing ±0.0001 g and a top-loading balance capable of weighing ±0.1 g.

4.5 Glassware

4.5.1 Bottle - 15 mL, screw cap, with Teflon cap liner.

4.5.2 Volumetric flasks - Class A with ground-glass stoppers.

4.5.3 Vials - 2 mL for GC autosampler.

4.6 Purge and trap device - The purge and trap device consists of three separate pieces of equipment; sample purger, trap, and desorber. Several complete devices are now commercially available.

4.6.1 The sample purger must be designed to accept 5-mL samples with a water column at least 3-cm deep. The gaseous head space between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles, each with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The sample purger, illustrated in Figure 2, meets these design criteria. Alternate sample purge devices may be used provided equivalent performance is demonstrated.

4.6.2 The trap must be at least 25-cm long and have an inside diameter of at least 0.105 in. The trap must be packed to contain the following minimum lengths of absorbents: 15 cm of 2,6-diphenylene oxide polymer (Tenax-GC 60/80 mesh) and 8 cm of silica gel (Davison Chemical, 35/60 mesh, grade 15, or equivalent). The minimum specifications for the trap are illustrated in Figure 3.

4.6.3 The desorber should be capable of rapidly heating the trap to 180°C. The polymer section of the trap should not be heated higher than 180°C and the remaining sections should not exceed 220°C during bakeout mode. The desorber design, illustrated in Figure 3, meets these criteria.

4.6.4 The purge and trap device may be assembled as a separate unit or be coupled to a gas chromatograph as illustrated in Figures 4 and 5.

4.6.5 A heater or heated bath capable of maintaining the purge device at 40°C ± 1°C.

4.7 GC/MS System

4.7.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, and gases.

4.7.2 Column - 6 ft long x 0.1 in. I.D. glass, packed with 1 percent SP-1000 on Carbopack B (60/80 mesh) or equivalent. Note: Capillary columns may be used for analysis of volatiles, as long as the analyst follows the analytical procedures in EPA Method 524.2, uses the internal standards and surrogates specified in this contract, and demonstrates that the analysis meets all of the performance and QA/QC criteria contained in this method.

4.7.3 Mass spectrometer - Capable of scanning from 35 to 260 amu every 3 s or less, using 70 V (nominal) electron energy in the electron-impact-ionization mode and producing a mass spectrum which meets all the criteria in Table 2 (see Section 8.0) when 50 ng of 4-bromofluorobenzene (BFB) is injected through the gas chromatograph inlet.

4.7.4 GC/MS interface - Any gas chromatograph to mass spectrometer interface that gives acceptable calibration points at 50 ng or less per injection for each of the parameters of interest and achieves all acceptable performance criteria (Section 9.0) may be used. Gas chromatograph to mass spectrometer interfaces constructed of all-glass or glass-lined materials are recommended. Glass can be deactivated by treating with dichlorodimethylsilane.

4.7.5 Data system - A computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits.

5.0 REAGENTS

5.1 Reagent water - Reagent water is defined as water in which an interferent is not observed at or above the CRDL of the analytes of interest.

5.1.1 Reagent water may be generated by passing tap water through a carbon filter bed containing about 453 g of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

5.1.2 A water purification system (Millipore Super-Q or equivalent) may be used to generate reagent water.

5.1.3 Reagent water may also be prepared by boiling water for 15 min. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant-free inert gas through the water for one hour. While still hot, transfer the water to a narrow-mouth screw-cap bottle and seal with a Teflon-lined septum and cap.

5.2 Sodium thiosulfate - (ACS) granular.

5.3 Methanol - Pesticide quality or equivalent.

5.4 Stock standard solutions - Stock standard solutions may be purchased or prepared from pure standard materials and must be traceable to standards supplied by EPA's Environmental Monitoring Systems Laboratory at Las Vegas (EMSL-LV). Prepare stock standard solutions in methanol using assayed liquids or gases, as appropriate.

5.4.1 Place about 9.8 mL of methanol into a 10.0-mL tared ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.4.2 Add the assayed reference material as described below.

5.4.2.1 Liquids - Using a 100-uL syringe, immediately add two or more drops of assayed reference material to the flask then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.4.2.2 Gases - To prepare standards for any of the four halocarbons that boil below 30°C (bromomethane, chloroethane, chloromethane, and vinyl chloride), fill a 5-mL valved, gas-tight syringe with the reference standard to the 5.0-mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas rapidly dissolves in the methanol. This may also be accomplished by using a lecture bottle equipped with a Hamilton Lecture Bottle Septum (no. 866600). Attach Teflon tubing to the side-arm relief valve and direct a gentle stream of gas into the methanol meniscus.

5.4.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in micrograms per micro-liter from the net gain in weight. When compound purity is assayed to be 96 percent or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared standards may be used at any concentration if they are certified by the manufacturer. Commercial standards must be traceable to standards supplied by EMSL-LV.

5.4.4 Transfer the stock standard solution into multiple Teflon-sealed, screw-cap bottles. Store with no headspace at -10°C to -20°C and protect from light. Once one of the bottles containing the standard solution has been opened, it may be used for at most one week.

5.4.5 Prepare fresh standards every two months for gases or for reactive compounds such as styrene. All other standards must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.5 Secondary dilution standards - Using stock standard solutions, prepare secondary dilution standards in methanol that contain the compounds of interest, either singly or mixed together. (See Section 9.0.) Secondary dilution standards should be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.6 Surrogate standard spiking solution - Prepare stock standard solutions for toluene-d_8, p-bromofluorobenzene, and 1,2-dichloroethane-d_4 in methanol as described in Section 5.4.

Prepare a surrogate standard spiking solution from these stock standards at a concentration of 250 ug/10 mL in methanol.

5.7 Matrix Spiking Solution

5.7.1 Prepare a spiking solution in methanol that contains the following compounds at a concentration of 250 ug/10 mL:

1,1-dichloroethene
trichloroethene
chlorobenzene
toluene
benzene

5.7.2 Matrix spikes also serve as duplicates; therefore, add an aliquot of this solution to each of two portions from one sample chosen for spiking.

5.8 BFB Standard - Prepare a 25-ng/uL solution of BFB in methanol.

5.9 Great care must be taken to maintain the integrity of all standard solutions. Store all standard solutions at -10°C to -20°C in screw-cap amber bottles with Teflon liners.

6.0 CALIBRATION

6.1 Assemble a purge and trap device that meets the specification in Section 4.6. Condition the trap overnight at 180°C in the purge mode with an inert gas flow of at least 20 cm^3/min. Daily, prior to use, condition the traps for 10 min while backflushing at 180°C with the column at 220°C.

6.2 Connect the purge and trap device to a gas chromatograph. The gas chromatograph must be operated using temperature and flow rate parameters equivalent to those in Section 7.1.2. Calibrate the purge and trap GC/MS system using the internal standard technique (Section 5.3).

6.3 Internal standard calibration procedure. The three internal standards are bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d_5, at 50 ug/L at time of purge.

6.3.1 Prepare calibration standards at a minimum of five concentration levels for each method parameter. The concentration levels are specified in Section 9.0. Aqueous standards may be stored up to 24 h, if held in sealed vials with zero headspace at -10°C to -20°C and protected from light. If not so stored, they must be discarded after one hour.

6.3.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Sections 5.4 and 5.5. It is recommended that the secondary dilution standard be prepared at a concentration of 25 ug/mL of each internal standard compound. The addition of 10 uL of this standard to 5.0 mL of sample or calibration standard would be equivalent of 50 ug/L.

6.3.3 Tune the GC/MS system to meet the criteria in Section 9.0 by injecting BFB. Analyze each calibration standard, according to Section 7.0, adding 10 uL of internal standard spiking solution directly to the syringe. Tabulate the area response of the characteristic ions against concentration for each compound and internal standard and calculate relative response factors (RRFs) for each compound using the following equation.

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$

where:

A_x = Area of the characteristic ion for the compound to be measured

A_{is} = Area of the characteristic ion for the specific internal standard from Section 9.0

C_{is} = Concentration of the internal standard

C_x = Concentration of the compound to be measured.

6.3.4 The average RRF must be calcu-lated for all compounds. A system performance check must be made before this calibration curve is used. Five compounds (the system performance check compounds, SPCC) are checked for a minimum average relative response factor. These SPCC are chloromethane, 1,1-dichloroethane, bromoform, 1,1,2,2-tetrachloroethane, and chlorobenzene. Six compounds (the calibration check compounds, CCC) are used to evaluate the curve. These CCC are 1,1-dichloroethene, chloroform, 1,2,-dichloropropane, toluene, ethylbenzene, and vinyl chloride. Calculate the percent relative standard deviati (%RSD) of RRF values over the working range of the curve. A minimum %RSD for each CCC must be met before the curve is valid.

$$\%RSD = \frac{\text{Standard deviation}}{\text{Mean}} \times 100$$

6.3.5 A check of the calibration curve must be performed once every 12 h. The minimum RRF for the SPCC must be checked. If this criterion is met, the RRFs of all compounds are calculated and reported. A percent difference of the daily RRF (12 h) compared to the average RRF from the initial curve is calculated. The maximum percent difference allowed for each CCC in Form VII (Figure 6) is checked. Only after both these criteria are met can sample analysis begin.

6.3.6 Internal standard responses and retention times in all standards must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 30 s from the latest daily (12 h) calibration standard, the chromatographic system must be inspected for malfunctions, and corrections made as required. The extracted ion current profile (EICP) of the internal standards must be monitored and evaluated for each standard. If the EICP area for any internal standard changes by more than a factor of two (-50 to +100 percent), the mass spectrometric system must be inspected for malfunction and corrections made as appropriate. When corrections are made, re-analysis of samples analyzed while the system was malfunctioning is necessary.

7.0 PROCEDURE

7.1 Instrumental Operating Conditions

7.1.1 Mass spectrometer

Electron Energy: 70 V (nominal)
Mass Range: 35 to 260 amu
Scan Time: to give at least 5 scans/
peak and not to exceed
3 s/scan.

7.1.2 Gas chromatograph - Column temperature should be held isothermal at 45°C for 3 min, then programmed at 8°C/min to 220°C and held for 15 min. Injector temperature is 200 to 225°C. Source temperature is set according to the manufacturer's specifications. Transfer line temperature is 250 to 300°C. The recommended carrier gas is helium at 30 cm^3/s. (See EPA Method 524.2 for capillary column conditions.)

7.1.3 After achieving the key ion abundance criteria, calibrate the system daily as described in Section 9.0.

7.1.4 Adjust the purge gas (helium) flow rate to 25 to 40 cm^3/min. Variations from this flow rate may be necessary to achieve better purging and collection efficiencies for some compounds, particularly chloromethane and bromoform.

7.2 Water Samples

7.2.1 All samples and standard solutions must be allowed to warm to ambient temperature before analysis.

7.2.2 Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample or standard bottle which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. This process of taking an aliquot destroys the validity of the sample for future analysis so if there is only one sample vial for volatiles organic analysis, the analyst should fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such a time when the analyst has determined that the first sample has been analyzed properly. Filling one 20-mL syringe would allow the use of only one syringe. If a second analysis is needed from the 20-mL syringe, it must be analyzed within 24 h. Care must also be taken to prevent air from leaking into the syringe.

7.2.3 The optional screening of hexadecane extracts for volatiles, if used, will have shown the approximate concentrations of major sample components. If a dilution of the sample was indicated, this dilution shall be made just prior to GC/MS analysis of the sample. All steps in the dilution procedure must be performed without delays until the point at which the diluted sample is in a gas-tight syringe. The following procedure will allow for dilutions near the calculated dilution factor from the screening procedure.

7.2.3.1 All dilutions are made in volumetric flasks (10 mL to 100 mL).

7.2.3.2 Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for extremely large dilutions.

7.2.3.3 Calculate the approximate volume of reagent water which will be added to the volumetric flask selected and add slightly less than this quantity of reagent water to the flask.

7.2.3.4 Inject the proper aliquot from the syringe prepared in Section 7.2.2 into the volumetric flask. Aliquots of less than 1-mL increments are prohibited. Dilute the flask to the mark with reagent water. Cap the flask, invert, and shake three times.

7.2.3.5 Fill a 5-mL syringe with the diluted sample as in Section 7.2.2.

7.2.3.6 If this is an intermediate dilution, use it and repeat above procedure to achieve larger dilutions.

7.2.4 Add 10.0 uL of the surrogate spiking solution (Section 5.6) and 10.0 uL of the internal standard spiking solution (Section 5.3.2) through the valve bore of the syringe, then close the valve. The surrogate and internal standards may

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be mixed and added as a single spiking solution. The addition of 10 uL of the surrogate spiking solution to 5 mL of sample is equivalent to a concentration of 50 ug/L of each surrogate standard.

7.2.5 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

7.2.6 Close both valves and purge the sample for 11.0 ± 0.1 min at ambient temperature.

7.2.7 At the conclusion of the purge time, attach the trap to the chromatograph, adjust the device to the desorb mode, and begin the gas chromatographic temperature program. Concurrently, introduce the trapped materials to the gas chromatographic column by rapidly heating the trap to 180°C while backflushing the trap with an inert gas between 20 to 60 cm^3/min for 4 min. If this rapid heating requirement cannot be met, the gas chromatographic column must be used as a secondary trap by cooling it to 30°C (or subambient, if problems persist) instead of the recommended initial temperature of 45°C.

7.2.8 While the trap is being desorbed into the gas chromatograph, empty the purging chamber. Wash the chamber with a minimum of two 5-mL flushes of reagent water to avoid carryover of pollutant compounds.

7.2.9 After desorbing the sample for 4 min, recondition the trap by returning the purge and trap device to the purge mode. Wait 15 s, then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 180°C. Trap temperatures up to 220°C may be employed, however the higher temperature will shorten the useful life of the trap. After approximately 7 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample.

7.2.10 If the initial analysis of a sample or a dilution of a sample has concentrations of method analytes that exceed the initial calibration range, the sample must be reanalyzed at a higher dilution. Secondary ion quantitation is only allowed when there are sample interferences with the primary ion. If secondary ion quantitation is used, document the reasons in the Case Narrative. When a sample is analyzed that contains saturated ions from a compound, this analysis must be followed by a blank reagent water analysis. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a blank can be analyzed that is free of interferences.

7.2.11 Add 10 uL of the matrix spiking solution (Section 5.7) to the 5 mL of sample purged. Disregarding any dilutions, this is equivalent to a concentration of 50 ug/L of each matrix spike standard.

7.2.12 All dilutions must keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

7.3 Soil/Sediment Samples

Two approaches may be taken to determine whether the low level or medium level method may be followed:

1. Assume the sample is low level and analyze a 5-g sample.

2. Use the X Factor calculated from the method for optional screening of hexadecane extracts for volatiles.

If peaks are saturated from the analysis of a 5-g sample, a smaller sample size must be analyzed to prevent saturation. However, the smallest sample size permitted is 1 g. If smaller than 1-g sample size is needed to prevent saturation, the medium level method must be used.

7.3.1 Low Level Soil Method

The low level soil method is based on purging a heated sediment/soil sample mixed with reagent water containing the surrogate and internal standards. Analyze all reagent blanks and standards under the same conditions as the samples.

Use 5 g of sample or use the X Factor to determine the sample size for purging.

1. If the X Factor is 0 (no peaks noted on the hexadecane screen), analyze a 5-g sample.
2. If the X Factor is between 0 and 1.0, analyze a minimum of a 1-g sample.

7.3.1.1 The GC/MS system should be set up as specified in Section 7.1. This should be done before preparing the sample to avoid loss of volatiles from standards and sample. A heated purge calibration curve must be prepared and used for the quantitation of all samples analyzed with the low level method. Follow the initial and daily calibration instructions except for the addition of a 40°C purge temperature.

7.3.1.2 To prepare the reagent water containing the surrogates and internal standards, remove the plunger from a 5-mL Luerlock syringe equipped with a syringe valve and fill until overflowing with reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 5.0 mL. Add 10 uL each of the surrogate spiking solution (Section 5.6) and the internal standard solution to the syringe through the valve. The surrogate and internal standards may be mixed and added as a single spiking solution. The addition of 10 uL of the surrogate spiking solution to 5 g of soil/sediment is equivalent to 50 ug/kg of each surrogate standard.

7.3.1.3 The sample consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. Weigh the amount determined in Section 7.3.1 into a tared purge device. Use a top loading balance. Note and record the actual weight to the nearest 0.1 g.

7.3.1.4 Immediately after weighing the sample, weigh 5 to 10 g of the sediment into a tared crucible. Determine the percent moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing. Concentrations of individual analytes will be reported relative to the dry weight of sediment.

Percent moisture =

$$\frac{\text{Weight of sample(g)} - \text{Weight of dry sample(g)}}{\text{Weight of sample (g)}} \times 100$$

7.3.1.5 Add the spiked reagent water to the purge device and connect the device to the purge and trap system. Note: Prior to the attachment of the purge device, Sections 7.3.1.2 and 7.3.1.3 must be performed rapidly to avoid loss of volatiles. These steps must be performed in a laboratory free of solvent fumes.

7.3.1.6 Heat the sample to 40°C ± 1°C and purge the sample for 11.0 ± 0.1 min.

7.3.1.7 Proceed with the analysis as outlined in Sections 7.2.7 to 7.2.10. Use 5 mL of the same reagent water as the reagent blank.

7.3.1.8 Add 10 uL of the matrix spiking solution (Section 5.7) to the 5 mL of water (Section 7.3.1.2). The concentration for a 5-g sample would be equivalent to 50 ug/kg of each matrix spike standard.

7.3.2 Medium Level Soil Method

The medium level soil method is based on extracting the soil/sediment sample with methanol. An aliquot of the methanol extract is added to reagent water containing the surrogate and internal standards. This is purged at ambient temperature. All samples with an X Factor >1.0 should be analyzed by the medium level method. If saturated peaks occurred or would occur when a 1-g sample was analyzed, the medium level method must be used.

7.3.2.1 The GC/MS system should be set up as specified in Section 7.1. This should be done prior to the addition of the methanol extract to reagent water.

7.3.2.2 The sample consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. Weigh 4 g (wet weight) into a tared 15-mL vial. Use a top loading balance. Note and record the actual weight to the nearest 0.1 g. Determine the percent moisture as in Section 7.3.1.4.

7.3.2.3 Quickly add 9.0 mL of methanol, then 1.0 mL of the surrogate spiking solution to the vial. Cap and shake for 2 min. Note: Sections 7.3.2.1 and 7.3.2.2 must be performed rapidly to avoid loss of volatiles. These steps must be performed in a laboratory free of solvent fumes.

7.3.2.4 Using a disposable pipet, transfer approximately 1 mL of extract into a GC vial for storage. The remainder may be disposed of. Transfer approximately 1 mL of the reagent methanol to a GC vial for use as the method blank for each case or set of 20 samples, whichever is more frequent. These extracts may be stored in the dark at 4°C (±2°C) prior to analysis.

The addition of a 100-uL aliquot of each of these extracts in Section 7.3.2.6 will give a concentration equivalent to 6200 ug/kg of each surrogate standard.

7.3.2.5 Use Table 1 to determine the volume of methanol extract to add to the 5 mL of reagent water for analysis. If the optional screening of hexadecane extracts was performed, use the X Factor (Option B) or the estimated concentration (Option A) to determine the appropriate volume. Otherwise, estimate the concentration range of the sample from the low level analysis to determine the appropriate volume. If the sample was submitted as a medium level sample, start with 100 uL.

All dilutions must keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve. Calculate appropriate dilution factor for concentrations exceeding this table.

Table 1. Volume of Methanol Extract to be Used for Analysis

X Factor	Estimated Concentration Range[a] (ug/kg)	Volume of Methanol Extract[b] (uL)
0.25 - 5.0	500 - 10,000	100
0.5 - 10.0	1000 - 20,000	50
2.5 - 50.0	5000 - 100,000	10
12.5 - 250.0	25,000 - 500,000	100 of 1/50 dilution[c]

a. Actual concentration ranges could be 10 to 20 times higher than this if the compounds are halogenated and the estimates are from GC/FID.

b. The volume of methanol added to the 5 mL of water being purged should be kept constant. Therefore, add to the 5 mL syringe whatever volume of methanol is necessary to maintain a volume of 100 uL added to the syringe.

c. Dilute an aliquot of the methanol extract and then take 100 uL for analysis.

7.3.2.6 Remove the plunger from a 5-mL Luerlock syringe equipped with a syringe valve and fill until overflowing with reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 4.9 mL. Pull the plunger back to 5 mL to allow volume for the addition of sample and standards. Add 10 uL of the internal standard solution. Also add the volume of methanol extract determined in Section 7.3.2.5 and a volume of methanol solvent to total 100 uL (excluding methanol in standards).

7.3.2.7 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valve and inject the water/methanol sample into the purging chamber.

7.3.2.8 Proceed with the analysis as outlined in Sections 7.2.6 to 7.2.10. Analyze all reagent blanks on the same instrument as the samples. The standards should also contain 100 uL of methanol to simulate the sample conditions.

7.3.2.9 For a matrix spike in the medium level sediment/soil samples, add 8.0 mL of methanol, 1.0 mL of surrogate spiking solution (Section 5.6), and 1.0 mL of matrix spiking solution (Section 5.7) in Section 7.3.2.2. This results in a 6200 ug/kg concentration of each matrix spike standard when added to a 4-g sample. Add a 100-uL aliquot of this extract to 5 mL of water for purging (as per Section 7.3.2.6).

7.4 Qualitative Analysis

7.4.1 The method analytes shall be identified by an analyst competent in the interpretation of mass spectra (by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound). Two criteria must be satisfied to verify the identifications: (1) elution of the sample component at the same GC relative retention time as the standard component, and (2) correspondence of the sample component and standard component mass spectra.

7.4.1.1 For establishing correspondence of the GC relative retention time (RRT), the sample component RRT must compare within ±0.06 RRT units of the RRT of the standard component. For reference, the standard must be run on the same shift as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using EICPs for ions unique to the component of interest.

7.4.1.2 For comparison of standard and sample component mass spectra, standard mass spectra obtained on the GC/MS system are required. Once obtained, these standard spectra may be used for identification purposes, only if the GC/MS system meets the daily tuning requirements for BFB. These standard spectra may be obtained from the run used to obtain reference RRTs.

7.4.1.3 The requirements for qualitative verification by comparison of mass spectra are as follows:

7.4.1.3.1 All ions present in the standard mass spectra at a relative intensity greater than 10 percent (most abundant ion in the spectrum equals 100 percent) must be present in the sample spectrum.

7.4.1.3.2 The relative intensities of ions specified in Section 7.4.1.3.1 must agree within plus or minus 20 percent between the standard and sample spectra. (Example: For an ion with an abundance of 50 percent in the standard spectra, the corresponding sample abundance must be between 30 and 70 percent.)

7.4.1.3.3 Ions greater than 10 percent in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. The verification process should favor false positives. All compounds meeting the identification criteria must be reported with their spectra. For all compounds below the CRDL, report the actual value followed by a "J", e.g., "3J."

7.4.1.4 If a compound cannot be verified by all of the criteria in Section 7.4.1.3, but in the technical judgment of the mass spectral interpretation specialist, the identification is correct, then the analyst shall report that identification and proceed with quantification in Section 8.0.

7.4.2 A library search shall be executed for non-method analytes for the purpose of tentative identification. For this purpose, the 1985 release of the National Bureau of Standards (NBS) Mass Spectral Library (or more recent release), containing 42,261 spectra, shall be used. Computer-generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

7.4.2.1 Up to ten non-method analytes of greatest apparent concentration shall be tentatively identified via a forward search of the NBS Mass Spectral Library. (Substances with responses less than 10 percent of the internal standard are not required to be searched in this fashion.) Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Computer-generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

7.4.2.2 Guidelines for making tentative identification:

1. Relative intensities of major ions in the reference spectrum (ions greater than 10 percent of the most abundant ion) should be present in the sample spectrum.

2. The relative intensities of the major ions should agree within ±20 percent. (Example: For an ion with an abundance of 50 percent of the standard spectra, the corresponding sample ion abundance must be between 30 and 70 percent.)

3. Molecular ions present in reference spectrum should be present in sample spectrum.

4. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

5. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or

Table 1. Examples of Orders of Elution of Pesticides/PCBs[a]

Analyte	Column 1	Column 2	Column 3
alpha-BHC	1.45	1.64	1.86
gamma-BHC	1.86	1.94	2.37
beta-BHC	2.18	1.76	2.75
Heptachlor	2.27	3.21	2.55
delta-BHC	2.55	2.01	2.80
Aldrin	2.76	4.01	2.93
Heptachlor epoxide	4.31	4.98	5.53
Endosulfan I	5.46	6.26	7.08
4,4'-DDE	6.37	7.51	6.03
Dieldrin	6.74	7.38	8.59
Endrin	8.25	8.35	10.14
4,4'-DDD	10.08	9.53	10.57
Endosulfan II	10.14	8.35	12.88
4,4'-DDT	12.06	12.75	11.55
Endrin aldehyde	13.64	9.53	21.11
Endosulfan sulfate	16.73	11.09	31.27
Endrin ketone	22.70	-	33.16
gamma Chlordane	4.77	5.74	5.25
alpha Chlordane	5.24	6.39	5.70
Toxaphene	mr	mr	mr
Aroclor-1016	mr	mr	mr
Aroclor-1221	mr	mr	mr
Aroclor-1232	mr	mr	mr
Aroclor-1242	mr	mr	mr
Aroclor-1248	mr	mr	mr
Aroclor-1254	mr	mr	mr
Aroclor-1260	mr	mr	mr
Methoxychlor	24.07	19.60	18.12
Dibutyl chlorendate	21.80	27.21	22.26

a. mr = Multiresponse compounds.

Column 1 conditions: Gas Chrom Q (80/100 mesh) or equivalent coated with 1.5 percent OV-17/1.95 percent OV-210 or equivalent packed in a 1.8-m long x 2-mm I.D. (6-mm O.D.) glass column with 5 percent methane/ 95 percent argon carrier gas at a flow rate of 30 mL/min. (HP 5880) Column temperature, isothermal at 192°C. 2-mm I.D. column with 80/100 mesh does not adequately resolve dibutylchlorendate and endrin ketone.

Column 2 conditions: Gas Chrom Q (100/120 mesh) or equivalent coated with 3 percent OV-1 or equivalent packed in a 1.8-m long x 2-mm I.D. (6-mm O.D.) glass column with 5 percent methane/95 percent argon carrier gas at a flow rate of 30 mL/min. (30 mL/min makeup gas). (Tracor 222.) Column temperature, isothermal at 194°C.

Column 3 conditions: Gas Chrom Q (80/100 mesh) or equivalent coated with 5 percent OV-210 packed in a 1.8-m x 2-mm I.D. (6-mm O.D.) glass

Table 1. Examples of Orders of Elution of Pesticides/PCBs (Continued)

column with 5 percent methane/95 percent argon carrier gas at a flow rate of 30 mL/min. (30 ml/min makeup gas). HP5840. Column temperature, isothermal at 183°C.

Capillary column 1 conditions: 30-m x 0.25-mm I.D., 0.25 micron film thickness, fused silica DB-5 (or equivalent) splitless mode
Helium carrier gas: 4 mL/min at 280°C and 25 psi
Septum purge: 15 mL/min
Split vent: none
Initial temperature: 160°C, initial hold - 2 min
Program at 5°C/min
Final temperature: 270°C, final hold - 4 min
Injection port temperature: 225°C

Capillary column 2 conditions: 10-m x 0.32-mm I.D., 1 micron film thickness, fused silica DB-1701, splitless mode
Helium carrier gas: 4 mL/min at 180°C and 25 psi
Septum purge: 15 mL/min
Split vent: none
Initial temperature: 160°C, initial hold - 3 min
Program at 10°C/min to 240°C
Program from 240 to 270°C at 5°C/min
Final hold: 4 min
Injection port temperature: 232°C

the analyst. If compound purity is certified at 96 percent or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are traceable by EPA's Environmental Monitoring System Laboratory - Las Vegas, Nevada (EMSL-LV) to standards supplied.

4.2.2 Transfer the stock standard solutions into a bottle/vial with Teflon-lined septa. Store at 4$0^{\circ}$C (±2°C) and protect from light. Stock standard solutions must be replaced after 12 months, or sooner if comparison with check standards indicates a problem.

4.3 Working standards solutions - Prepare mixtures of standards diluted with hexane that will provide approximately half-scale response for all the compounds of interest. This should be at the attenuation setting capable of achieving the contract required detection limits (Table D-3). (This would be approximately 0.01 ng/uL for aldrin.) All individual component standards must be in two mixtures for packed column. One mixture is acceptable when using capillary. Include dibutylchlorendate in all the standard mixtures. All multicomponent standards--i.e., PCB Aroclors and toxaphene--must be in separate solutions with the exception of Aroclors 1016/1260. Include dibutylchlorendate in all multicomponent standard mixtures.

4.3.1 Evaluation standard mixtures - Prepare working standard mixtures diluted with hexane containing aldrin, endrin, 4,4'-DDT, and dibutylchlorendate to evaluate the GC column. Prepare three concentration levels to provide the following criteria.

4.3.1.1 Low level will be approximately 20 percent above base line (Evaluation Standard Mixture A).

4.3.1.2 Mid level will be approximately half scale (Evaluation Standard Mixture B).

9 2 1 2 4 7 0 7 2 1

4.3.1.3 High level will be approximately full scale (Evaluation Standard Mixture C). (Dibutylchlorendate must be 0.1 ng/uL to correspond with 100 percent surrogate recovery in 10-mL final volume. This may be slightly greater than full scale but should still be in linear range.)

4.3.2 Individual standard mixtures - These include all single component pesticide method parameters plus alpha chlordane, gamma chlordane, endrin ketone, endrin aldehyde and dibutylchlorendate (see Section 6.1.4 for suggested mixtures). Alpha and gamma chlordane should be in Mixture B to avoid overlap with other pesticides.

5.0 CALIBRATION

5.1 The gas chromatographic system must be calibrated using the external standard technique for all packed columns used for quantitation.

5.2 External Standard Calibration Procedure

5.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with hexane. One of the external standards should be at a concentration near, but above, the contract required determination limit (CRDL) and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector. This should be done on each quantitation column and each instrument at the beginning of the contract period and each time a new column is installed. The data must be retained by the laboratory and made available for inspection during on-site evaluations.

5.2.2 Using injections of 2 to 5 uL of each calibration standard, tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each compound.

6.0 GC/EC PRIMARY ANALYSIS

Adjust oven temperature and carrier gas flow rates so that the retention time for 4,4'-DDT is equal to or greater than 12 min.

Table 1 provides examples of operating conditions for the gas chromatograph. Separation should be ≥25 percent resolution between peaks. Percent resolution is calculated by dividing the height of the valley by the peak height of the smaller peak being resolved, multiplied by 100. This criterion must be considered when determining whether to quantitate on the primary analysis or the confirmation analysis. When this criterion cannot be met, quantitation is adversely affected because of the difficulty in determining where to establish the baseline.

6.1 Inject 2 to 5 uL of the sample or standard extract using the solvent-flush technique or autosampler. Smaller (1.0 uL) volumes can be injected only if automatic devices are employed. Record the volume injected to the nearest 0.05 uL and the total extract volume. Note: Dibutylchlorendate recovery may be calculated from a capillary or packed column GC/EC meeting all quality control (QC) requirements for quantitation. However, matrix spike duplicates must be quantitated on a packed column.

6.1.1 Inject Individual Standard Mixtures A and B and all multiresponse pesticides/PCBs at the beginning of each 72-h sequence (see Section 6.1.3.5). To establish the retention time (RT) window within each 72-h sequence for the pesticide/PCB of interest, use the absolute RT from the above chromatograms as the mid-point, and ±3 times the standard deviation calculated in Section 9.4 for each compound. Individual Standard Mixtures A and B are analyzed alternately and intermittently throughout the analysis as shown in Section 6.1.3.5. Any pesticide outside of its established retention time window requires immediate investigation and correction before continuing the analysis. The laboratory must re-analyze all affected samples.

6.1.2 Sample analysis of extracts can begin when linearity and degradation quality assurance/quality control (QA/QC) requirements specified in Section 9.0 have been met. Note: The 10.0 percent relative standard deviation (RSD) linearity criterion is only required on the column(s) being used for pesticide/PCBs quantitation. If a column is used for surrogate quantitation only, the 10.0 percent RSD is required only for dibutylchlorendate.

Analyze samples in groups of no more than five samples. After the analysis of the first group of up to five samples, analyze Evaluation Mixture B. Analyze another group of up to five samples, followed by the analysis of Individual Mix A or B. Subsequent groups of up to 5 samples may be analyzed by repeating this sequence, alternately analyzing Evaluation Mixture B and Individual Mixture A or B between the groups as shown in Section 6.1.3.5. The pesticide/PCB analytical sequence must end with Individual Mixture A and B regardless of the number of samples analyzed (see Section 6.1.3.5).

If a multiresponse pesticide/PCB is detected in either of the preceding groups of five samples, the appropriate multiresponse pesticide/PCB may be substituted for Individual Mixtures A or B. All standards listed in Section 6.1.3.5 must be included for every case and must be analyzed within the same 72-h period as the samples, with the exception of Aroclors 1221 and 1232 which are analyzed at a minimum of once per month (see footnotes in Section 6.1.3.5). If the samples are split between two or more instruments, the complete set of standards must be analyzed on each instrument with the same 72-h requirement. All standards must be analyzed prior to the samples to avoid the effects of poor chromatography caused by the unsuspected injection of a highly concentrated sample.

6.1.3 Sections 6.1.3.1 to 6.1.3.5 contain GC performance criteria. If it is determined during the course of a 72-h sequence that one or more of the criteria have been violated, stop the run and take corrective action (see Section 9.0). After the corrective action has been taken, the 72-h sequence may be restarted as follows. If a standard violated the criterion, restart the sequence with that standard, determine that the criteria have been met, and continue with sample analyses, according to Section 6.1.3.5. If a sample violated the criterion, restart the sequence with the standard that would have followed that group of samples (thereby preserving the sequence of standards in Section 6.1.3.5), determine that the criteria have been met, and continue with sample analyses, according to 6.1.3.5.

If it is determined after the completion of a 72-h sequence that one or more of the criteria have been violated, proceed as follows. If a standard violated the criterion, all samples analyzed after that standard must be re-analyzed as part of a new 72-h sequence. If a subsequent standard in the original sequence met all the criteria, then only those samples analyzed between the standard that did not meet the criterion and the standard that did meet the criterion must be re-analyzed as part of a new 72-h sequence. If only samples violated the criteria, then those samples must be re-analyzed as part of a new 72-h sequence.

6.1.3.1 Differences in the calibration factors for each standard in Individual Standard Mixtures A and B must not exceed 20.0 percent (15.0 percent for any standard compound used for quantitation) during the 72-h primary analysis. Calculate the percent difference using the initial Individual Standard Mix versus all subsequent Individual Standard Mixtures analyzed during the 72-h sequence. (The equations for calculation of calibration factor and percent difference are in Section 9.0.)

The retention time shift of dibutylchlorendate in any standard or sample must be less than 2.0 percent for packed columns (<0.3 percent for capillary columns).

6.1.3.2 Samples must also be repeated if the degradation of DDT and/or endrin exceeds 20.0 percent respectivel on the intermittent analysis of Evaluation Standard Mixture B.

6.1.3.3 All pesticide standards must fall within the established 72-h retention time windows.

6.1.3.4 Highly colored extracts may require a dilution.

6.1.3.5 The 72-h sequence must be as follows.

1. Evaluation Standard Mixture A
2. Evaluation Standard Mixture B
3. Evaluation Standard Mixture C
4. Individual Standard Mixture A*
5. Individual Standard Mixture B*

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*These may be combined into one mixture for capillary column analyses.

6. Toxaphene
7. Aroclors 1016/1260
8. Aroclor 1221**
9. Aroclor 1232**
10. Aroclor 1242
11. Aroclor 1248
12. Aroclor 1254
13. 5 samples
14. Evaluation Standard Mixture B
15. 5 samples
16. Individual Standard Mixtures A or B
17. 5 samples
18. Evaluation Standard Mixture B
19. 5 samples
20. Individual Standard Mixture A or B (whichever not run in step 16)
21. 5 samples
22. Repeat the above sequence starting with Evaluation Standard Mixture B
23. Pesticide/PCB analysis sequence must end with Individual Standard Mixtures A and B regardless of number of samples analyzed.

6.1.4 Suggested groups of compounds and concentrations for Individual Standard Mixtures A and B follow, which are recommended to prevent overlap of compounds on the two packed columns (3 percent OV-1 and 1.5 percent OV-17/1.95 percent OV-210). Some of the compounds overlap on the 5 percent OV-210 column (see Table 1). The concentration is based on a 5-uL injection.

**Aroclors 1221 and 1232 must be analyzed on each instrument and each column at a minimum of once per month. Copies of these chromatograms must be submitted for sample analyses performed during the applicable month.

Individual Standard Mixture A		Individual Standard Mixture B	
Compound	Concentration (ng/uL)	Compound	Concentration (ng/uL)
gamma-BHC	0.005	alpha-BHC	0.005
heptachlor	0.010	beta-BHC	0.010
aldrin*	0.010	delta-BHC	0.010
heptachlor epoxide	0.010	aldrin*	0.010
endosulfan I	0.010	4,4'-DDE	0.010
dieldrin	0.010	endrin	0.010
4,4'-DDT	0.020	4,4'-DDD	0.020
endrin aldehyde	0.025	endosulfan sulfate	0.020
endosulfan II	0.020	endrin ketone	0.020
methoxychlor	0.100	alpha chlordane	0.010
dibutylchlorendate	0.050	gamma chlordane	0.010
		dibutylchlorendate	0.050

*For RRT determination.

6.1.5 Inject the method blank (extracted with each set of samples) on every instrument and GC column on which the samples are analyzed.

6.2 Evaluation of Chromatograms

6.2.1 Consider the sample negative when its peaks, depending on the pesticide's response factor, result in concentrations less than the required quantitation level. The sample is complete at this point. Confirmation is not required.

6.2.2 Tentative identification is made when the unknown's retention time matches the retention time of a corresponding standard that was chromatographed on the same instrument within a 72-h period.

coeluting compounds. Data system library reduction programs can sometimes create these discrepancies.

7.4.2.3 If in the technical judgment of the mass spectral interpretation specialist, no valid tentative identification can be made, the compound should be reported as unknown. The mass spectral specialist should give additional classification of the unknown compound, if possible (i.e. unknown aromatic, unknown hydrocarbon, unknown acid type, unknown chlorinated compound). If probable molecular weights can be distinguished, include them.

8.0 CALCULATIONS

8.1 Method analytes identified shall be quantified by the internal standard method. The internal standard used shall be that which is listed in Table 5. The EICP area of the characteristic ions of analytes listed in Tables 2 and 3 are used.

8.2 Internal standard responses and retention times in all standards must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 30 s from the latest daily (12 h) calibration standard, the chromatographic system must be inspected for malfunctions, and corrections made as required. The internal standard EICPs must be monitored and evaluated for each sample, blank, matrix spike, and matrix spike duplicate. If the EICP area for any internal standard changes by more than a factor of two (-50 to +100 percent), the mass spectrometric system must be inspected for malfunction and corrections made as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is necessary.

Table 2. Characteristic Ions for Surrogate and Internal Standards

Compound	Primary Ion	Secondary Ion(s)
SURROGATE STANDARDS		
4-Bromofluorobenzene	95	174, 176
1,2-Dichloroethane-d_4	65	102
Toluene-d_8	98	70, 100
INTERNAL STANDARDS		
Bromochloromethane	128	49, 130, 51
1,4-Difluorobenzene	114	63, 88
Chlorobenzene-d_5	117	82, 119

Table 3. Characteristic Ions for Volatile Compounds

Parameter	Primary Ion[a]	Secondary Ion(s)
Chloromethane	50	52
Bromomethane	94	96
Vinyl chloride	62	64
Chloroethane	64	66
Methylene chloride	84	49, 51, 86
Acetone	43	58
Carbon disulfide	76	78
1,1-Dichloroethene	96	61, 98
1,1-Dichloroethane	63	65, 83, 85, 98, 100
1,2-Dichloroethene	96	61, 98
Chloroform	83	85
1,2-Dichloroethane	62	64, 100, 98
2-Butanone	72	57
1,1,1-Trichloroethane	97	99, 117, 119
Carbon tetrachloride	117	119, 121
Vinyl acetate	43	86
Bromodichloromethane	83	85
1,1,2,2-Tetrachloroethane	83	85, 131, 133, 166
1,2-Dichloropropane	63	65, 114
trans-1,3-Dichloropropene	75	77
Trichloroethene	130	95, 97, 132
Dibromochloromethane	129	208, 206
1,1,2-Trichloroethane	97	83, 85, 99, 132, 134
Benzene	78	-
cis-1,3-Dichloropropene	75	77
Bromoform	173	171, 175, 250, 252, 254, 256
2-Hexanone	43	58, 57, 100
4-Methyl-2-pentanone	43	58, 100
Tetrachloroethene	164	129, 131, 166
Toluene	92	91
Chlorobenzene	112	114
Ethyl benzene	106	91
Styrene	104	78, 103
Total xylenes	106	91

a. The primary ion should be used unless interferences are present, in which case, a secondary ion may be used.

8.2.1 If after re-analysis the EICP areas for all internal standards are inside the contract limits (-50 to +100 percent), the problem with the first analysis is considered to have been within the control of the laboratory. Therefore, only submit data from the analysis with EICPs within the contract limits. This is considered the initial analysis and must be reported as such on all data deliverables.

8.2.2 If the re-analysis of the sample does not solve the problem (i.e., the EICP areas are outside the contract limits for both analyses), submit the EICP data and sample data from both analyses. Distinguish between the initial analysis and the re-analysis on all data deliverables. Document in the Case Narrative all inspection and corrective actions taken.

8.3 The relative response factor (RRF) from the daily standard analysis is used to calculate the concentration in the sample. Use the relative response factor as determined in Section 6.3.3 and the equations below. When method analytes are below contract required detection limits (CRDL) but the spectra meet the identification criteria, report the concentration with a "J". For example, if CRDL is 10 ug/L and concentration of 3 ug/L is calculated, report as "3J".

Water

$$\text{Concentration (ug/L)} = \frac{(A_x)(I_s)}{(A_{is})(RRF)(V_o)}$$

where:

A_x = Area of the characteristic ion for the compound to be measured

A_{is} = Area of the characteristic ion for the internal standard

I_s = Amount of internal standard added (ng)

V_o = Volume of water purged, accounting for dilutions (mL).

Sediment/Soil (Medium Level)

$$\text{Concentration (ug/kg)} = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RRF)(V_i)(W_s)(D)}$$

Sediment/Soil (Low Level)

$$\begin{array}{l}\text{Concentration (ug/kg)}\\ \text{(dry weight basis)}\end{array} = \frac{(A_x)(I_s)}{(A_{is})(RRF)(W_s)(D)}$$

where:

A_x, I_s, A_{is} = Same as for water, above

V_t = Volume of total extract (uL) (Use 10,000 uL or a factor of this when dilutions are made.)

V_i = Volume of extract added for purging (uL)

$D = \frac{100 - \text{percent moisture}}{100}$

W_s = Weight of sample extracted or purged (g).

8.4 An estimated concentration for non-method analytes tentatively identified shall be quantified by the internal standard method. For quantification, the nearest internal standard free of interferences shall be used.

8.4.1 The formula for calculating concentrations is the same as in Section 8.3. Total area counts (or peak heights) from the total ion chromatograms are to be used for both the compound to be measured and the internal standard. A relative response factor (RRF) of one (1) is to be assumed. The value from this quantitation shall be qualified as estimated. This estimated concentration should be calculated for all tentatively identified compounds as well as those identified as unknowns.

8.4.2 Xylenes (o, m, and p isomers) are to be reported as xylenes (total). Since o- and p-xylene overlap, the xylenes must be quantitated as m-xylene. The concentration of all xylene isomers must be added together to give the total.

8.4.3 1,2-Dichloroethene (trans and cis stereoisomers) are to be reported as 1,2-dichloroethene (total). The concentrations of both isomers must be added together to give the total.

8.5 Calculate surrogate standard recovery on all samples, blanks and spikes. Determine if recovery is within limits and report on appropriate form.

8.5.1 Calculation for surrogate recovery.

$$\text{Percent surrogate recovery} = \frac{Q_d}{Q_a} \times 100\%$$

where:

Q_d = Quantity determined by analysis

Q_a = Quantity added to sample.

8.5.2 If recovery is not within limits, the following is requi[illegible]:

1. Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.

2. Re-analyze the sample if none of the above reveal a problem.

8.5.3 If the re-analysis of the sample solves the problem, the problem was within the laboratory's control. Therefore, only submit data from the analysis with surrogate spike recoveries within the contract limits. This shall be considered the initial analysis and shall be reported as such on all data deliverables.

8.5.4 If the re-analysis of the sample does not solve the problem (i.e., surrogate recoveries are outside the contract limi[illegible] for both analyses), submit the surrogate spike recovery da[illegible] and the sample data from both analyses. Distinguish between the initial analysis and the re-analysis on all data deliverables.

8.5.5 If the sample with surrogate recoveries outside the limits is the sample used for the matrix spike and matrix spike duplicate, and the surrogate recoveries of the matrix spike and matrix spike duplicate show the same pattern (i.e., outside the limits), the sample, matrix spike, and matrix spike duplicate do not require re-analysis. Document in the narrative the similarity in surrogate recoveries.

9.0 QUALITY ASSURANCE/QUALITY CONTROL

9.1 Tuning and GC/MS Mass Calibration

It is necessary to establish that a given GC/MS meets the standard mass spectral abundance criteria prior to initiating any on-going data collection. This is accomplished through the analysis of p-bromofluorobenzene (BFB).

Definition: The 12-h time period for GC/MS system tuning and standards calibration (initial or continuing calibration criteria) begins at the moment of injection of the BFB analysis that the laboratory submits as documentation of a compliant tune. The time period ends after 12 h has elapsed according to the system clock.

9.1.1 Each GC/MS system used for the analysis of volatiles must be hardware tuned to meet the abundance criteria listed in Table 4 for a maximum of a 50-ng injection of BFB. Alternately, add 50 ng of BFB solution to 5.0 mL of reagent water and analyze according to Section 7.0. BFB shall not be analyzed simultaneously with any calibration standards or blanks. This criterion must be demonstrated daily or for each 12-h time period, whichever is more frequent. If required, background subtraction must be straightforward and designed only to eliminate column bleed or instrument background ions. Background subtraction actions resulting in spectral distortions for the sole purpose of meeting the contract specifications are unacceptable.

Note: All instrument conditions must be identical to those used in sample analysis, except that a different temperature program may be used.

9.1.2 BFB criteria must be met before any standards, samples, or blanks are analyzed. Any samples analyzed when tuning criteria have not been met may require re-analysis.

Table 4. BFB Key Ions and Abundance Criteria

Mass	Ion Abundance Criteria
50	15.0 - 40.0 percent of the base peak
75	30.0 - 60.0 percent of the base peak
95	base peak, 100 percent relative abundance
96	5.0 - 9.0 percent of the base peak
173	less than 2.0 percent of mass 174
174	greater than 50.0 percent of the base peak
175	5.0 - 9.0 percent of mass 174
176	greater than 95.0 percent but less than 101.0 percent of mass 174
177	5.0 - 9.0 percent of mass 176

9.1.3 Whenever the analyst takes corrective action which may change or affect the tuning criteria for BFB (e.g., ion source cleaning or repair, etc.), the tune must be verified irrespective of the 12-h tuning requirements.

9.1.4 Calibration should be documented in the form of a bar graph spectrum and as a mass listing.

Form V (GC/MS Tuning and Mass Calibration, Figure 7) should be completed each time an analytical system is tuned. In addition, all standards, samples, blanks, matrix spikes, and matrix spike duplicates analyzed during a particular tune must be summarized in chronological order on the bottom of the appropriate Form V. Detailed instructions for the completion of Form V can be found in the Contract Laboratory Program (CLP) Statement of Work for Organics Analysis.

9.2 Initial Calibration of the GC/MS System

Prior to the analysis of samples and required blanks and after tuning criteria have been met, the GC/MS system must be initially calibrated at a minimum of five concentrations to determine the linearity of response using method analyte standards. Once the system has been calibrated, the calibration must be verified each 12-h time period for each GC/MS system.

9.2.1 Prepare calibration standards as described in Section 5.0 containing the method parameters at 20, 50, 100, 150 and 200 ug/L. Surrogate and internal standards shall be used with each of the calibration standards. This will result in 100 to 1000 total ng analyzed. If an analyte saturates at the 200 ug/L concentration level, and the GC/MS system is calibrated to achieve a detection sensitivity of no less than 5 ug/L, the analyst should calculate the results based on a four-point initial calibration for the specific analyte that saturates. The use of separate calibration methods which reflect the two different low and medium soil/sediment methods is required. Secondary ion quantitation is only allowed when there are sample interferences with the primary ion. If secondary ion quantitation is used, document the reasons in the Case Narrative. Analyze all method blanks and standards under the same conditions as the samples.

9.2.2 The U.S. EPA plans to develop performance-based criteria for response factor data acquired during this program. To accomplish this goal, the U.S. EPA has specified both the concentration levels for initial calibration and the specific internal standard to be used on a compound-by-compound basis for quantitation (see Table 5). Establishment of standard calibration procedures is necessary and deviations will not be allowed.

9.2.3 Analyze each calibration standard and tabulate the area of the primary characteristic ion against concentration for each compound including all contract required surrogate compounds. The relative retention times of each compound in each calibration run should agree within 0.06 relative retention time units. Late eluting compounds usually will have much better agreement.

Table 5. Volatile Internal Standards with Corresponding Method Analytes Assigned for Quantification

Bromochloromethane	1,4-Difluorobenzene	Chlorobenzene-d_5
Chloromethane	2-Butanone	2-Hexanone
Bromomethane	1,1,1-Trichloroethane	4-Methyl-2-Pentanone
Vinyl Chloride	Carbon Tetrachloride	Tetrachloroethene
Chloroethane	Vinyl Acetate	1,1,2,2-Tetrachloroethane
Methylene Chloride	Bromodichloromethane	Toluene
Acetone	1,2-Dichloropropane	Chlorobenzene
Carbon Disulfide	trans-1,3-Dichloropropene	Ethylbenzene
1,1-Dichloroethene	Trichloroethene	Styrene
1,1-Dichloroethane	Dibromochloromethane	Xylene(total)
1,2-Dichloroethene(total)	1,1,2-Trichloroethane	Bromofluorobenzene[a]
Chloroform	Benzene	Toluene-d_8[a]
1,2-Dichloroethane	cis-1,3-Dichloropropene	
1,2-Dichloroethane-d_4[a]	Bromoform	

a. Surrogate compound.

Using Table 5 and the following equation, calculate the relative response factors (RRF) for each compound at each concentration level.

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$

where:

A_x = Area of the characteristic ion for the compound to be measured

A_{is} = Area of the characteristic ion for the specific internal standards from Table 5 or 6

C_{is} = Concentration of the internal standard (ng/uL)

C_x = Concentration of the compound to be measured (ng/uL).

Using the relative response factors (RRF) from the initial calibration, calculate the percent relative standard deviations (%RSD) for compounds labeled on Form VI (Volatile Organics Initial Calibration Data, Figure 8) as calibration check compounds (CCC) and shown in Table 6 using the following equation.

$$\%RSD = \frac{SD}{\bar{x}} \times 100$$

where:

SD = Standard deviation of initial relative response factors (per compound)

$\bar{x}$ = Mean of initial relative response factors (per compound).

SD can be calculated from the following equation.

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(x_i - \bar{x})^2}{N-1}}$$

where:

N = Number of relative response factors

X_i = Initial relative response factor.

The %RSD for each CCC must be less than or equal to 30.0 percent. This criterion must be met for the initial calibration to be valid.

9.2.4 A system performance check must be performed to ensure that minimum average relative response factors are met before the calibration curve is used.

9.2.4.1 The five system performance check compounds (SPCCs) are chloromethane, 1,1-dichloroethane, bromoform, 1,1,2,2-tetrachloroethane and chlorobenzene. The minimum acceptable average relative response factor (RRF) for these compounds is 0.250 for bromoform and 0.300 for the other four SPCC. These compounds typically have RRFs of 0.4 to 0.6 and are used to check compound instability and check for degradation caused by contaminated lines or active sites in the system. For instance,

1. Chloromethane - This compound is the most likely compound to be lost if the purge flow is too fast.

2. Bromoform - This compound is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response. Response of the quantitation ion (m/z 173) is directly affected by the tuning of BFB at ions m/z 174/176. Increasing the m/z 174/176 ratio may improve bromoform response.

3. Tetrachloroethane, 1,1-Dichloroethane - These compounds can be deteriorated by contaminated transfer lines in purge and trap systems and/or active sites in trapping materials.

9.2.4.2 The initial calibration is valid only after both the %RSD for CCC and the minimum RRF for SPCC have been met. Only after both these criteria are met can sample analysis begin.

9.2.5 Once the initial calibration is validated, calculate and report the average relative response factor (RRF) and percent relative standard deviation (%RSD) for all method analytes. Complete Form V and Form VI (Figures 7 and 8) for each instrument used to analyze samples under this protocol. Detailed instructions for completion of these forms can be found in the CLP Statement of Work for Organics Analysis.

9.3 Continuing Calibration of GC/MS System

A calibration standard(s) containing all method analytes including all required surrogates, must be performed each 12-h time period during analysis. Compare the relative response factor data from the standards each 12 h with the average relative response factor from the initial calibration for a specific instrument. A system performance check must be made each 12 h. If the SPCC criteria are met, a comparison of relative response factors is made for all compounds. This is the same check that is applied during the initial calibration (Form VI, Figure 8). If the minimum relative response factors are not met, the system must be evaluated and corrective action must be taken before sample analysis begins.

9.3.1 Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatography system. This check must be met before analysis begins. The minimum RRF for the SPCCs is 0.300 (0.250 for bromoform).

9.3.2 After the system performance check is met, CCCs listed in Table 6 are used to check the validity of the initial calibration. Calculate the percent difference using the following equation.

$$\text{Percent difference} = \frac{RRF_I - RRF_c}{RRF_I} \times 100$$

where:

RRF_I = Average relative response factor from initial calibration

RRF_C = Relative response factor from current calibration check standard.

If the percent difference for any compound is greater than 20 percent, the laboratory should consider this a warning limit. If the percent difference for each CCC is less than or equal to 25.0 percent, the initial calibration is assumed to be valid. If the criteria are not met (>25.0 percent difference), for any one calibration check compound, corrective action must be taken. Problems similar to those listed under SPCC could affect this criteria. If no source of the problem can be determined after corrective action has been taken, a new initial five-point calibration must be generated. These criteria must be met before sample analysis begins.

Table 6. Volatile Calibration Check Compounds

1,1-Dichloroethene
Chloroform
1,2-Dichloropropane
Toluene
Ethylbenzene
Vinyl Chloride

9.3.3 The U.S. EPA plans to evaluate the long term stability of relative response factors during this program. Standardization among contract laboratories is necessary to reach these long term goals. Along with contract-specified concentrations for initial calibration, the U.S. EPA is requiring specific concentrations for each continuing calibration standard(s). The concentration for each method parameter in the continuing calibration standard(s) is 50 ug/L.

9.3.4 Complete and submit Form VII (Volatile Continuing Calibration Data, Figure 6) for each GC/MS system used for each 12-h time period. Calculate and report the relative response factor and percent difference for all compounds. Ensure that the minimum RRF is 0.300 for volatile SPCCs and 0.250 for bromoform. The percent difference for each CCC must be less than or equal to 25.0 percent. Additional instructions for completing Form VII can be found in the CLP Statement of Work for Organics Analysis.

9.4 Method Blank Analysis

A method blank is a volume of deionized, distilled laboratory water for water samples, or a purified solid matrix for soil/sediment samples, carried through the entire analytical scheme. The method blank volume or weight must be approximately equal to the sample volumes or sample weights being processed.

9.4.1 For the analysis of volatile method analytes, a method blank analysis must be performed once for each 12-h time period during the analysis of samples from:

1. Each Case, or
2. Each 14-calendar-day period during which samples in a case are received (said period beginning with the receipt of the first sample in that Sample Delivery Group), or
3. Each 20 samples in a Case that are of similar matrix (water or soil) or similar concentration (soil only),

whichever is most frequent, on each GC/MS system used to analyze samples.

9.4.2 It is the analyst's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be minimized.

9.4.3 For the purposes of this protocol, an acceptable laboratory method blank should meet the criteria of Sections 9.4.3.1 and 9.4.3.2.

9.4.3.1 A method blank for volatile analysis must contain no greater than five times the CRDL of methylene chloride, acetone, toluene, and 2-butanone.

9.4.3.2 For all other method analytes not listed above, the method blank must contain less than the CRDL of any single analyte.

9.4.3.3 If a laboratory method blank exceeds these criteria, the analyst must consider the analytical system to be out of control. The source of the contamination must be investigated and appropriate corrective measures must be taken and documented before further sample analysis proceeds. All samples processed with a method blank that is out of control (i.e., contaminated) must be re-extracted/repurged and re-analyzed.

9.4.4 Report results of method blank analysis using Form I and Form I, TIC (see Figures 9 and 10). In addition, the samples associated with each method blank must be summarized on Form IV (Volatile Method Blank Summary, Figure 11). Detailed instructions for the completion of these forms can be found in the CLP Statement of Work for Organics Analysis. Sample concentration data shall be reported for blanks.

9.5 Surrogate Spike Analysis

Surrogate standard determinations are performed on all samples and blanks. All samples and blanks are fortified with surrogate spiking compounds before purging or extraction to monitor preparation and analysis of samples.

9.5.1 Each sample, matrix spike, matrix spike duplicate, and blank are spiked with surrogate compounds prior to purging or extraction. The surrogate spiking compounds shown in Table 7 are used to fortify each sample, matrix spike, matrix spike duplicate, and blank with the proper concentrations. Performance based criteria are generated from laboratory results. Therefore, deviations from the spiking protocol will not be permitted.

Table 7. Surrogate Spiking Compounds

Compounds	Fraction	Amount in Sample Extract[a] Water	Low/Medium Soil
Toluene-d_8	VOA	50 ug	50 ug
4-Bromofluorobenzene	VOA	50 ug	50 ug
1,2-Dichloroethane-d_4	VOA	50 ug	50 ug

a. At the time of injection, before any optional dilutions.

9.5.2 Surrogate spike recovery must be evaluated by determining whether the concentration (measured as percent recovery) falls inside the contract required recovery limits listed in Table 8.

9.5.3 Method Blank Surrogate Spike Recovery

The laboratory must take the actions listed below if recovery of any one surrogate compound in the volatiles fraction of the method blank is outside of the required surrogate spike recovery limits.

Table 8. Contract Required Recovery Limits for Surrogate Spikes

Surrogate Compound	Water	Low/Medium Soil
Toluene-d_8	88-110	81-117
4-Bromofluorobenzene	86-115	74-121
1,2-Dichloroethane-d_4	76-114	70-121

9.5.3.1 Check calculations to ensure that there are no errors; check internal standard and surrogate spiking solutions for degradation, contamination, etc; also check instrument performance.

9.5.3.2 Re-analyze the blank or extract if steps in Section 9.5.3.1 fail to reveal the cause of the noncompliant surrogate recoveries.

9.5.3.3 If the blank is a methanol extract for medium level soil samples, re-extract and re-analyze the blank if steps in Section 9.5.3.2 fail to reveal the cause of the noncompliant surrogate recoveries.

9.5.3.4 If the measures listed in Sections 9.5.3.1 to 9.5.3.3 fail to correct the problem, the analytical system must be considered out of control. The problem must be corrected before continuing. This may mean recalibrating the instrumentation but it may also mean more extensive action. The specific corrective action is left up to the GC/MS operator. When surrogate recovery(ies) in the blank is outside of the contract required windows, all samples associated with that blank must be re-analyzed.

9.5.4 Sample Surrogate Spike Recovery

The laboratory must take the actions listed below if recovery of any one surrogate compound in the volatiles fraction of the sample is outside of the contract surrogate spike recovery limits.

9.5.4.1 The laboratory shall document (in this instance, document means to write down and discuss problem and corrective action taken) deviations outside of acceptable quality control limits by taking the following actions:

9.5.4.1.1 Check calculations to ensure that there are no errors; check internal standard and surrogate spiking solutions for degradation, contamination, etc; also check instrument performance.

9.5.4.1.2 If the steps in Section 9.5.4.1.1 fail to reveal a problem, then reanalyze the sample or extract. If re-analysis of the sample or extract solves the problem, the problem was within the laboratory's control. Therefore, only submit data from the analysis with surrogate spike recoveries within the contract windows. This shall be reported as such on all data deliverables.

9.5.4.1.3 If the sample was soil extracted with methanol and the steps in Section 9.5.4.1.2 fail to solve the problem, then re-extract and re-analyze the sample. If the re-extraction and re-analysis solves the problem, the problem was in the laboratory's control. Therefore, only submit data from the extraction and analysis with surrogate spike recoveries within the contract windows. This shall be considered the initial analysis and shall be reported as such on all data deliverables.

If the re-extraction and/or re-analysis of the sample does not solve the problem (i.e., surrogate recoveries are outside the contract windows for both analyses), submit the surrogate spike recovery data and the sample data from both analyses according to Section 9.5.5. Distinguish between the initial analysis and the re-analysis on all data deliverables.

9.5.5 Report surrogate recovery data for the following:

1. Method blank analysis
2. Sample analysis
3. Matrix spike/matrix spike duplicate analyses
4. All sample re-analyses that substantiate a matrix effect.

The surrogate spike recovery data are summarized on Form II (Figures 12 and 13) (Surrogate Spike Percent Recovery Summary). Detailed instructions for the completion of Form II can be found in the CLP Statement of Work for Organic Analysis.

9.6 Matrix Spike/Matrix Spike Duplicate Analysis

To evaluate the matrix effect of the sample upon the analytical methodology, the matrix spiking solution (Section 5.7) should be used for matrix spike and matrix spike duplicate analyses. These compounds in the matrix spiking solution are subject to change depending upon availability and suitability for use as matrix spikes.

9.6.1 A matrix spike analysis and matrix spike duplicate analysis must be performed for each group of samples of a similar matrix, once per:

1. Each case of field samples received, or
2. Each 20 field samples in a case, or
3. Each group of samples of a similar concentration level (soils only), or
4. Each 14-calendar-day period during which samples in a case were received (said period beginning with the receipt of the first sample in that Sample Delivery Group),

whichever is most frequent.

9.6.2 The amount of matrix spiking solution to be added to the sample aliquots is stipulated in Section 7.0. Each method allows for optional dilution steps which must be accounted for when calculating percent recovery of the matrix spike and matrix spike duplicate samples. Samples requiring optional dilutions and chosen as the matrix spike/matrix spike duplicate samples, must be analyzed at the same dilution as the original unspiked sample.

9.6.3 Individual component recoveries of the matrix spike are calculated using the following equation.

$$\text{Matrix spike percent recovery} = \frac{SSR - SR}{SA} \times 100$$

where:

SSR = Spike sample results

SR = Sample result

SA = Spike added from spiking mix.

9.6.4 Calculate the relative percent difference (RPD) between the matrix spike and matrix spike duplicate using the following equation.

$$RPD = \frac{|D_1 - D_2|}{(D_1 + D_2)/2} \times 100$$

where:

D_1 = First sample value

D_2 = Second sample value (duplicate).

9.6.5 The matrix spike results (concentrations) for nonspiked method analytes shall be reported on Form I (Organic Analysis Data Sheet, Figure 9) and the matrix spike percent recoveries shall be summarized on Form III (MS/MSD Recovery, Figures 14 and 15). These values will be used by EPA to periodically update existing performance-based QC recovery limits (Table 9).

The results for nonspiked method analytes in the matrix spike duplicate analysis shall be reported on Form I (Organic Analysis Data Sheet, Figure 9) and the percent recovery and the relative percent difference shall be summarized on Form III (MS/MSD Recovery, Figures 14 and 15). The RPD data will be used by EPA to evaluate the long-term precision of the analytical method. Detailed instructions for the completion of Form III can be found in the CLP Statement of Work for Organics Analysis.

Table 9. Matrix Spike Recovery Limits

Matrix Spike Compound	Water	Soil/Sediment
1,1-Dichloroethene	61-145	59-172
Trichlorethene	71-120	62-137
Chlorobenzene	75-130	60-133
Toluene	76-125	59-139
Benzene	76-127	66-142

9.7 QC Activities Involved with Sample Analysis

The intent of Section 9.7 is to provide the analyst with a brief summary of ongoing QC activities involved with sample analysis. Specific references are provided to help the analyst meet specific reporting and deliverables requirements.

9.7.1 Samples can be analyzed upon successful completion of the initial QC activities. When 12 h have elapsed since the initial tune was completed, it is necessary to conduct an instrument tune and calibration check analysis (Section 9.2). Any major system maintenance, such as a source cleaning or installation of a new column, may necessitate a retune and recalibration irrespective of the 12-h requirement. Minor maintenance should necessitate only continuing calibration verification (Section 9.3).

9.7.2 Internal Standards Evaluation - Internal standard responses and retention times in all samples must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 s, the chromatographic system must be inspected for malfunctions, and corrections made as required. The extracted ion current profile (EICP) of the internal standards must be monitored and evaluated for each sample, blank, matrix spike, and matrix spike duplicate. If the EICP area for any internal standard changes by more than a factor of two (-50 to +100 percent), from the latest daily (12-h time period) calibration standard, the mass spectrometric system must inspected for malfunction, and corrections made as appropriate. Breaking off 1 ft of the column or cleaning the injector sleeve will often improve high-end sensitivity for the late eluting compounds; repositioning or repacking the front end of the column will often improve front end column performance. Poor injection technique can also lead to variable internal standard ratios. When corrections are made, re-analysis of samples analyzed while the system was malfunctioning is necessary.

9.7.2.1 If after re-analysis, the EICP areas for all internal standards are inside the contract limits (-50 to +100 percent), the problem with the first analysis is considered to have been within the control of the laboratory. Therefore, only submit data from the analysis with EICPs within the contract limits. This is considered the initial analysis and must be reported as such on all data deliverables.

9.7.2.2 If the re-analysis of the sample does not solve the problem (i.e., the EICP areas are outside the contract limits for both analyses), submit the EICP data and sample data from both analyses. Distinguish between the initial analysis and the re-analysis on all data deliverables. Document in the Case Narrative all inspection and corrective actions taken.

9.7.3 Each analytical run must also be checked for saturation. The level at which an individual compound will saturate the detection system is a function of the overall system sensitivity and the mass spectral characteristics of that compound. The initial method calibration (Section 9.2) requires that the system should not be saturated for high response compounds at 200 ug/L for method analytes.

9.7.3.1 If any compound in any sample exceeds the initial calibration range, that sample must be diluted, the internal standard concentration re-adjusted, and the sample re-injected, as described in Section 7.0. Secondary ion quantitation is only allowed when there are sample matrix interferences with the primary ion. If secondary ion quantitation is performed, document the reasons.

9.7.3.2 If the dilution of the sample causes any compound detected in the first analysis to be undetectable in the second analysis, the results of both analyses shall be reported on separate Forms I (Figure 9).

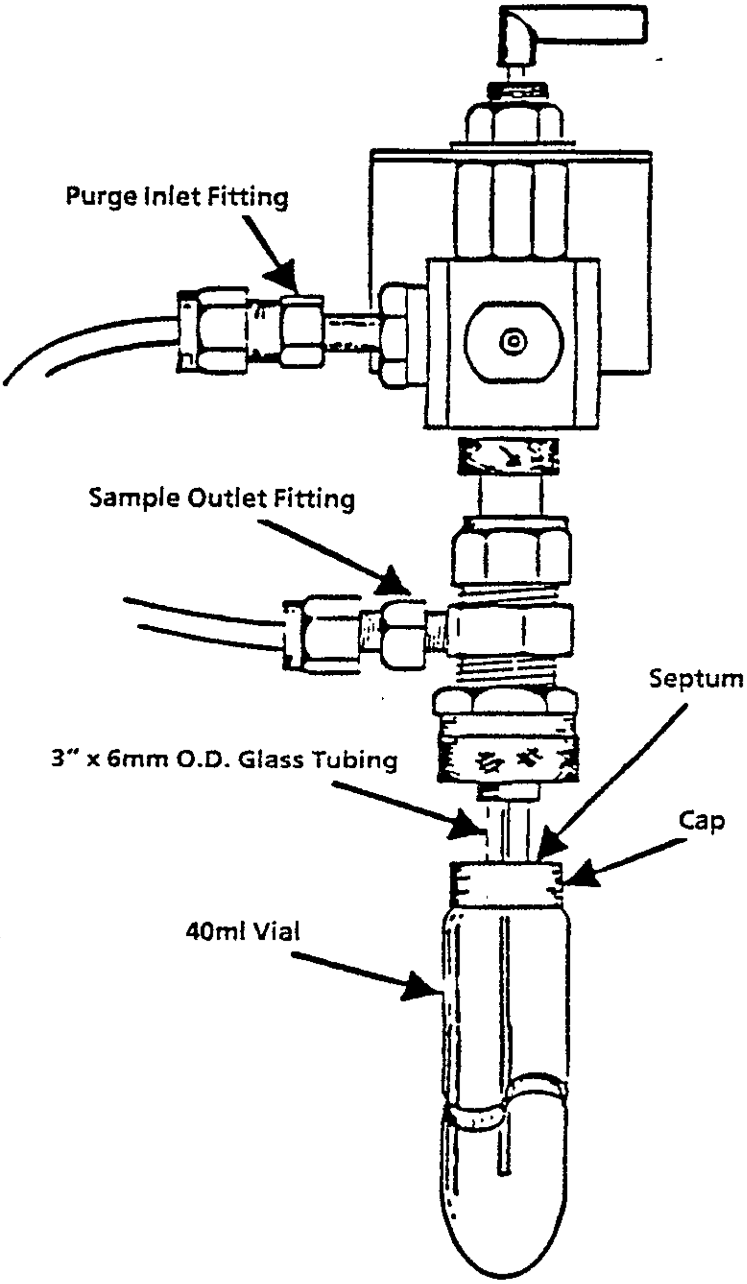
Purge Inlet Fitting
Sample Outlet Fitting
Septum
3" x 6mm O.D. Glass Tubing
Cap
40ml Vial

Figure 1. Low Soils Impinger

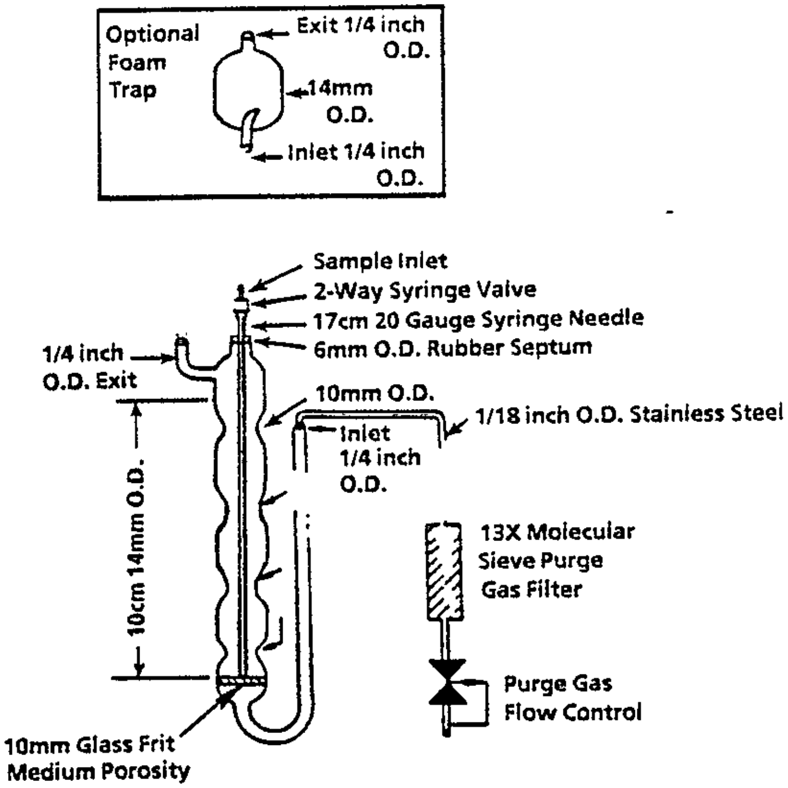
Optional
Foam
Trap
Exit 1/4 inch O.D.
14mm O.D.
Inlet 1/4 inch O.D.
Sample Inlet
2-Way Syringe Valve
17cm 20 Gauge Syringe Needle
6mm O.D. Rubber Septum
1/4 inch O.D. Exit
10mm O.D.
1/18 inch O.D. Stainless Steel
Inlet 1/4 inch O.D.
10cm 14mm O.D.
13X Molecular Sieve Purge Gas Filter
Purge Gas Flow Control
10mm Glass Frit Medium Porosity

Figure 2. Purging Device

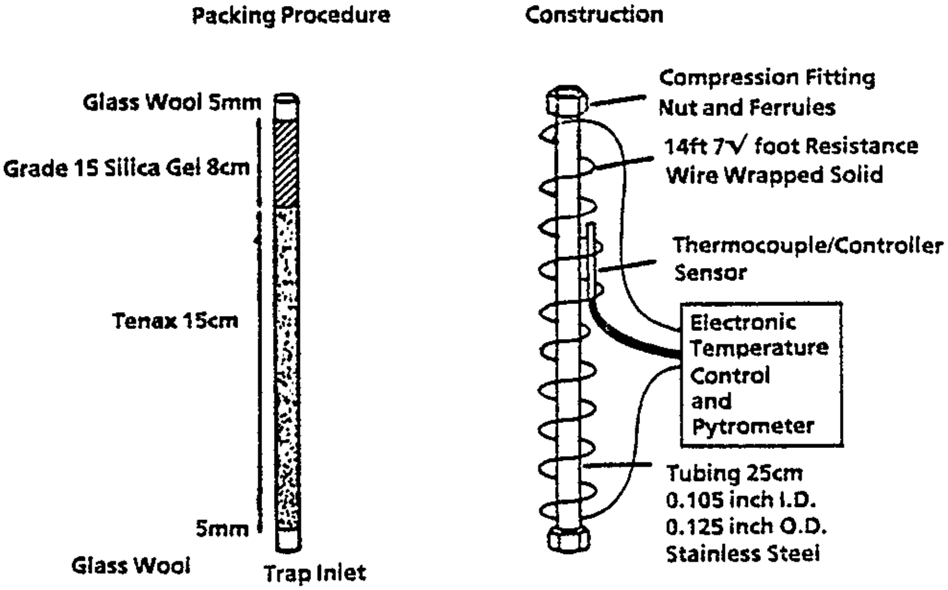
Packing Procedure
Construction
Glass Wool 5mm
Grade 15 Silica Gel 8cm
Tenax 15cm
5mm
Glass Wool
Trap Inlet
Compression Fitting Nut and Ferrules
14ft 7√ foot Resistance Wire Wrapped Solid
Thermocouple/Controller Sensor
Electronic Temperature Control and Pytrometer
Tubing 25cm 0.105 inch I.D. 0.125 inch O.D. Stainless Steel

Figure 3. Trap Packings and Construction To Include Desorb Capability

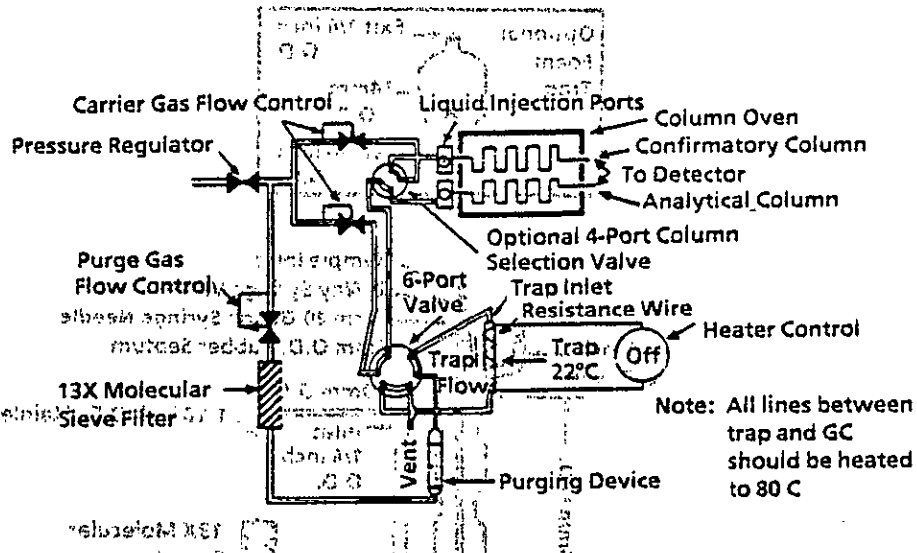
Carrier Gas Flow Control
Liquid Injection Ports
Column Oven
Pressure Regulator
Confirmatory Column
To Detector
Analytical Column
Optional 4-Port Column Selection Valve
Purge Gas Flow Control
6-Port Valve
Trap Inlet
Resistance Wire
Heater Control
Trap
Trap 22°C
Off
Flow
13X Molecular Sieve Filter
Note: All lines between trap and GC should be heated to 80 C
Vent
Purging Device

Figure 4. Schematic of Purge and Trap Device — Purge Mode

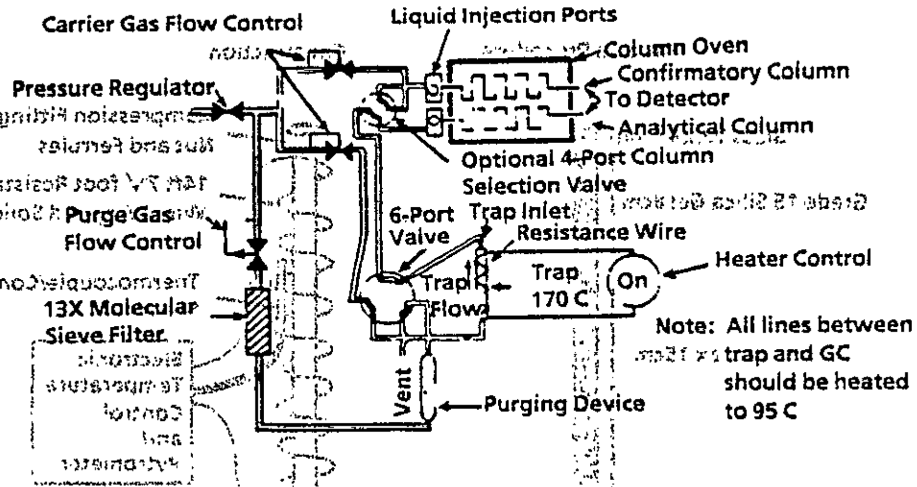
Carrier Gas Flow Control
Liquid Injection Ports
Column Oven
Confirmatory Column
Pressure Regulator
To Detector
Analytical Column
Optional 4-Port Column Selection Valve
Purge Gas Flow Control
6-Port Valve
Trap Inlet
Resistance Wire
Heater Control
Trap
Trap 170 C
On
Flow
13X Molecular Sieve Filter
Note: All lines between trap and GC should be heated to 95 C
Vent
Purging Device

Figure 5. Schematic of Purge and Trap Device — Desorb Mode

VOLATILE CONTINUING CALIBRATION DATA

Lab Name: ______________________ Contract: __________

Lab Code: ________ Case No.: ______ SAS No.: ________ SDG No.: ________

Instrument ID: __________ Calibration Date(s): __________ Time: ________

Lab File ID: __________ Init. Calib. Date(s): __________

Minimum RRF50 for SPCC(#) is 0.300 (0.250 for Bromoform)

Maximum % D for CCC(*) is 25.0%

COMPOUND	RRF	RRF50	%D
Chloromethane	#		
Bromomethane			
Vinyl Chloride	*		*
Chloroethane			
Methylene Chloride			
Acetone			
Carbon Disulfide			
1,1-Dichloroethene	*		*
1,1-Dichloroethane	#		
1,2-Dichloroethene (total)			
Chloroform	*		*
1,2-Dichloroethane			
2-Butanone			
1,1,1-Trichloroethane			
Carbon Tetrachloride			
Vinyl Acetate			
Bromodichloromethane			
1,2-Dichloropropane	*		*
cis-1,3-Dichloropropene			
Trichloroethene			
Dibromochloromethane			
1,1,2-Trichloroethane			
Benzene			
Trans-1,3-Dichloropropene			
Bromoform	#		
4-Methyl-2-Pentanone			
2-Hexanone			
Tetrachloroethene			
1,1,2,2-Tetrachloroethane	#		
Toluene	*		*
Chlorobenzene	#		
Ethylbenzene	*		*
Styrene			
Xylene (total)			
Toluene-d_8			
Bromofluorobenzene			
1,2-Dichloroethane-d_4			

FORM VII 10/86

Figure 6. Volatile Continuing Calibration Data

VOLATILE ORGANIC GC/MS TUNING AND MASS CALIBRATION - BROMOFLUOROBENZENE (BFB)

Lab Name: ____________________ Contract: ____________
Lab Code: ________ Case No.: ________ SAS No.: ________ SDG No.: ________
Lab File ID: ____________ BFB Injection Date: ____________
Instrument ID: ____________ BFB Injection Time: ____________

m/e	ION ABUNDANCE CRITERIA	% RELATIVE ABUNDANCE
50	15.0 - 40.0% of the base peak	
75	30.0 - 60.0% of the base peak	
95	Base peak, 100% relative abundance	
96	5.0 - 9.0% of the base peak	
173	Less than 2.0% of mass 174	
174	Greater than 50.0% of the base peak	( )1
175	5.0 - 9.0% of mass 174	( )1
176	Greater than 95.0%, but less than 101.0% of mass 174	( )1
177	5.0 - 9.0% of mass 176	( )2

1-Value is % mass 174 2-Value is % mass 176

THIS TUNE APPLIES TO THE FOLLOWING SAMPLES, MS, MSD, BLANKS, AND STANDARDS

	EPA SAMPLE NO.	LAB SAMPLE ID	LAB FILE ID	DATE OF ANALYSIS	TIME OF ANALYSIS
01					
02					
03					
04					
05					
06					
07					
08					
09					
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					
21					
22					
23					
24					

Page ___ of ___ FORM V 10/86

Figure 7. Volatile Organic GC/MS Tuning and Mass Calibration — Bromofluorobenzene

VOLATILE ORGANICS INITIAL CALIBRATION DATA

Lab Name: ____________________ Contract: __________

Lab Code: ______ Case No.: ______ SAS No.: ______ SDG No.: ______

Instrument ID: ________ Calibration Date(s): ________ ________

Minimum $\overline{RRF}$ for SPCC(#) is 0.300 (0.250 for Bromoform)

Maximum % RSD for CCC(*) is 30.0%

LAB FILE ID: ________ RRF20 = ________ RRF50 = ________

RRF100= ________ RRF150= ________ RRF200= ________

COMPOUND		RRF20	RRF50	RRF100	RRF150	RRF200	$\overline{RRF}$	% RSD
Chloromethane	#							
Bromomethane								
Vinyl Chloride	*							*
Chloroethane								
Methylene Chloride								
Acetone								
Carbon Disulfide								
1,1-Dichloroethene	*							*
1,1-Dichloroethane	#							
1,2-Dichloroethene (total)								
Chloroform	*							*
1,2-Dichloroethane								
2-Butanone								
1,1,1-Trichloroethane								
Carbon Tetrachloride								
Vinyl Acetate								
Bromodichloromethane								
1,2-Dichloropropane	*							*
cis-1,3-Dichloropropene								
Trichloroethene								
Dibromochloromethane								
1,1,2-Trichloroethane								
Benzene								
Trans-1,3-Dichloropropene								
Bromoform	#							
4-Methyl-2-Pentanone								
2-Hexanone								
Tetrachloroethene								
1,1,2,2-Tetrachloroethane	#							
Toluene	*							*
Chlorobenzene	#							
Ethylbenzene	*							*
Styrene								
Xylene (total)								
Toluene-d_8								
Bromofluorobenzene								
1,2-Dichloroethane-d_4								

Page ___ of ___ FORM VI 10/86

Figure 8. Volatile Organics Initial Calibration Data

VOLATILE ORGANICS ANALYSIS DATA SHEET

EPA SAMPLE NO.

Lab Name: ________ Contract: ________
Lab Code: ________ Case No.: ________ SAS No.: ________ SDG No.: ________
Matrix: (soil/water) ________ Lab Sample ID: ________
Sample wt/Vol: ________ (g/mL) ________ Lab File ID: ________
Level: (low/med) ________ Date Received: ________
% Moisture: not dec. ________ Date Analyzed: ________
Dilution Factor: ________

CAS NO.	COMPOUND	CONCENTRATION UNITS: (ug/L or ug/kg) ________	Q
74-87-3	Chloromethane		
74-83-9	Bromomethane		
75-01-4	Vinyl Chloride		
75-00-3	Chloromethane		
75-09-2	Methylene Chloride		
67-64-1	Acetone		
75-15-0	Carbon Disulfide		
75-35-4	1,1-Dichloroethene		
75-34-3	1,1-Dichloroethane		
540-59-0	1,2-Dichloroethene (total)		
67-66-3	Chloroform		
107-06-2	1,2-Dichloroethane		
78-93-3	2-Butanone		
71-55-6	1,1,1-Trichloroethane		
56-23-5	Carbon Tetrachloride		
108-05-4	Vinyl Acetate		
75-27-4	Bromodichloromethane		
78-87-5	1,2-Dichloropropane		
10061-01-5	cis-1,3-Dichloropropene		
79-01-6	Trichloroethene		
124-48-1	Dibromochloromethane		
79-00-5	1,1,2-Trichlorethane		
71-43-2	Benzene		
10061-02-6	trans-1,3-Dichloropropene		
75-25-2	Bromoform		
108-10-1	4-Methyl-2-Pentanone		
591-78-6	2-Hexanone		
127-18-4	Tetrachloroethene		
79-34-5	1,1,2,2-Tetrachloroethane		
108-88-3	Toluene		
108-90-7	Chlorobenzene		
100-41-4	Ethylbenzene		
100-42-5	Styrene		
133-02-7	Xylene (total)		

FORM I 10/86

Figure 9. Volatile Organics Analysis Data Sheet

VOLATILE ORGANICS ANALYSIS DATA SHEET
TENTATIVELY IDENTIFIED COMPOUNDS

EPA SAMPLE NO.

____

Lab Name: ______________ Contract: ______________

Lab Code: ______ Case No.: ______ SAS No.: ______ SDG No.: ______

Matrix: (soil/water) ______ Lab Sample ID: ______________

Sample wt/vol: ______ (g/mL) ______ Lab File ID: ______________

Level: (low/med) ______ Date Received: ______________

% Moisture: not dec. ______ Date Analyzed: ______________

Dilution Factor: ______________

CONCENTRATION UNITS:

Number TICs found: ______ (ug/L or ug/kg) ______

	CAS NUMBER	COMPOUND NAME	RT	EST. CONC.	Q
1.					
2.					
3.					
4.					
5.					
6.					
7.					
8.					
9.					
10.					
11.					
12.					
13.					
14.					
15.					
16.					
17.					
18.					
19.					
20.					
21.					
22.					
23.					
24.					
25.					
26.					
27.					
28.					
29.					
30.					

FORM I TIC 10/86

Figure 10. Volatile Organics Analysis Data Sheet, Tentatively Identified Compounds

VOLATILE METHOD BLANK SUMMARY

Lab Name: ______________________ Contract: ____________
Lab Code: ________ Case No.: ______ SAS No.: ______ SDG No.: ______
EPA Sample No. for Method Blank: ______ Lab Sample ID: ______
Instrument ID: ____________ Lab File ID: ______
Date Analyzed: ____________ Time Analyzed: ______
Matrix: (soil/water) ______ Level: (low/med) ______

THIS METHOD BLANK APPLIES TO THE FOLLOWING SAMPLES, MS AND MSD:

	EPA SAMPLE NO.	LAB SAMPLE ID	LAB FILE ID	TIME OF ANALYSIS
01				
02				
03				
04				
05				
06				
07				
08				
09				
10				
11				
12				
13				
14				
15				
16				
17				
18				
19				
20				
21				
22				
23				
24				
25				
26				
27				
28				
29				
30				

COMMENTS: ____________________________________

Page ___ of ___ FORM IV 10/8

Figure 11. Volatile Method Blank Summary

WATER VOLATILE SURROGATE RECOVERY

Lab Name: ____________ Contract: ____________
Lab Code: ______ Case No.: ______ SAS No.: ______ SDG No.: ______

	EPA SAMPLE NO.	S1 (TOL)#	S2 (BFB)#	S3 (DCE)#	OTHER	TOT OUT
01						
02						
03						
04						
05						
06						
07						
08						
09						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						
26						
27						
28						
29						
30						

		QC LIMITS
S1 (TOL)	= Toluene-d_8	(88-110)
S2 (BFB)	= Bromofluorobenzene	(86-115)
S3 (DCE)	= 1,2-Dichloroethane-d_4	(76-114)

#Column to be used to flag recovery values with an asterisk

*Values outside of contract required QC limits

Page ___ of ___ FORM II 10/86

Figure 12. Water Volatile Surrogate Recovery

SOIL VOLATILE SURROGATE RECOVERY

Lab Name: ______________ Contract: ____________
Lab Code: ________ Case No.: ________ SAS No.: ________ SDG No.: ________
Level: (low/med) ________

	EPA SAMPLE NO.	S1 (TOL)#	S2 (BFB)#	S3 (DCE)#	OTHER	TOT OUT
01						
02						
03						
04						
05						
06						
07						
08						
09						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						
26						
27						
28						
29						
30						

		QC LIMITS
S1 (TOL)	= Toluene-d_8	(81-117)
S2 (BFB)	= Bromofluorobenzene	(74-121)
S3 (DCE)	= 1,2-Dichloroethane-d_4	(70-121)

# Column to be used to flag recovery values with an asterisk

*Values outside of contract required QC limits

Page ___ of ___

FORM II

Figure 13. Soil Volatile Surrogate Recovery

WATER VOLATILE MATRIX SPIKE/MATRIX SPIKE DUPLICATE RECOVERY

Lab Name: ______________ Contract: ______________
Lab Code: ________ Case No.: ________ SAS No.: ________ SDG No.: ________
Matrix Spike - EPA Sample No.: ________

COMPOUND	AMOUNT ADDED (ng)	SAMPLE CONC. (ug/L)	MS CONC. (ug/L)	MS% REC	QC LIMITS REC.
1,1-Dichloroethene					61-145
Trichloroethene					71-120
Benzene					76-127
Toluene					76-125
Chlorobenzene					75-130

COMPOUND	MSD CONC. (ug/L)	MSD% REC	MS% REC #	% RPD #	QC LIMITS	
					RPD	REC.
1,1-Dichloroethene					14	61-145
Trichloroethene					14	71-120
Benzene					14	76-127
Toluene					14	76-125
Chlorobenzene					14	75-130

# Column to be used to flag recovery and RPD values with an asterisk

*Values outside of QC limits

RPD: ________ out of ________ outside limits
Spike Recovery: ________ out of ________ outside limits

COMMENTS: ____________________________________

FORM III 10/86

Figure 14. Water Volatile Matrix Spike/Matrix Spike Duplicate Recovery

SOIL VOLATILE MATRIX SPIKE/MATRIX SPIKE DUPLICATE RECOVERY

Lab Name: ____________________ Contract: ____________
Lab Code: __________ Case No.: ________ SAS No.: ________ SDG No.: ________
Matrix Spike - EPA Sample No.: __________ Level: (low/med) ______

COMPOUND	AMOUNT ADDED (ng)	SAMPLE CONC. (ug/L)	MS CONC. (ug/L)	MS% REC	QC LIMITS REC.
1,1-Dichloroethene					59-172
Trichloroethene					62-137
Benzene					66-142
Toluene					59-139
Chlorobenzene					60-133

COMPOUND	MSD CONC. (ug/L)	MSD% REC#	MS% REC#	% RPD #	QC LIMITS	
					RPD	REC.
1,1-Dichloroethene					24	59-172
Trichloroethene					24	62-137
Benzene					21	66-142
Toluene					21	59-139
Chlorobenzene					21	60-133

# Column to be used to flag recovery and RPD values with an asterisk
*Values outside of QC limits

RPD: ________ out of ________ outside limits
Spike Recovery: ________ out of ________ outside limits

COMMENTS: ____

FORM III 10/86

Figure 15. Soil Volatile Matrix Spike/Matrix Spike Duplicate Recovery

VOLATILE INTERNAL STANDARD AREA SUMMARY

Lab Name: ____________________ Contract: __________ __________
Lab Code: ________ Case No.: ______ SAS No.: ________ SDG No.: ________
EPA Sample No.(Standard): ________ Date Analyzed: ____________
Lab File ID (Standard): ________ Time Analyzed: ____________
Instrument ID: ________

		IS1 (BCM) AREA #	RT	IS2 (DFB) AREA #	RT	IS3 (CBZ) AREA #	RT
	12 HOUR STD						
	UPPER LIMIT						
	LOWER LIMIT						
	EPA SAMPLE NO.						
01							
02							
03							
04							
05							
06							
07							
08							
09							
10							
11							
12							
13							
14							
15							
16							
17							
18							
19							
20							
21							
22							
23							
24							

IS1 (BCM) = Bromochloromethane
IS2 (DFB) = 1,4-Difluorobenzene
IS3 (CBZ) = Chlorobenzene

UPPER LIMIT = + 100% of internal standard area.
LOWER LIMIT = - 50% of internal standard area.

# Column used to flag internal standard area values with an asterisk

Page ___ of ___ FORM VIII 10/86

Figure 16. Volatile Internal Standard Area Summary

SEMIVOLATILE ORGANIC COMPOUNDS

The analytical methods that follow are designed to analyze water, soil and sediment for the semivolatile organic compounds (semivolatiles) listed in Table D-2. The methods are derived from the U.S. EPA's Contract Laboratory Program (CLP) Statement of Work for Organics Analysis (October, 1986).

The methods include the following: sample preparation, screening, and analysis. Sample preparation covers sample extraction and cleanup techniques. As described in the screening section, a portion of the extracts may be screened on a gas chromatograph with appropriate detectors to determine the concentration level of organics. The analysis method involves GC/MS techniques for the determination of the semivolatiles; it is based on EPA Method 625 (Base/Neutrals and Acids).

Problems have been associated with the following compounds covered by this method. Dichlorobenzidine and 4-chloroaniline can be subject to oxidative losses during solvent concentration. This is especially true in the soil/sediment method when concentrating the methylene chloride/acetone extraction solvent. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition. N-nitrosodiphenylamine decomposes in the gas chromatographic inlet forming diphenylamine and, consequently, cannot be separated from diphenylamine native to the sample.

Table D-2. Analytes Determined by CLP Semivolatiles Analysis Method

		Contract Required Detection Limits[a]	
Analyte	CAS Number	Water (ug/L)	Low Soil/Sediment[b,c] (ug/kg)
35. Phenol	108-95-2	10	330
36. bis(2-Chloroethyl) ether	111-44-4	10	330
37. 2-Chlorophenol	95-57-8	10	330
38. 1,3-Dichlorobenzene	541-73-1	10	330
39. 1,4-Dichlorobenzene	106-46-7	10	330
40. Benzyl alcohol	100-51-6	10	330
41. 1,2-Dichlorobenzene	95-50-1	10	330
42. 2-Methylphenol	95-48-7	10	330
43. bis(2-Chloroisopropyl)ether	39638-32-9	10	330
44. 4-Methylphenol	106-44-5	10	330
45. N-Nitroso-dipropylamine	621-64-7	10	330
46. Hexachloroethane	67-72-1	10	330
47. Nitrobenzene	98-95-3	10	330
48. Isophorone	78-59-1	10	330
49. 2-Nitrophenol	88-75-5	10	330
50. 2,4-Dimethylphenol	105-67-9	10	330
51. Benzoic acid	65-85-0	50	1600
52. bis(2-Chloroethoxy) methane	111-91-1	10	330
53 2,4-Dichlorophenol	120-83-2	10	330
54. 1,2,4-Trichlorobenzene	120-82-1	10	330
55. Naphthalene	91-20-3	10	330
56. 4-Chloroaniline	106-47-8	10	330
57. Hexachlorobutadiene	87-68-3	10	330
58. 4-Chloro-3-methylphenol (para-chloro-meta-cresol)	59-50-7	10	330
59. 2-Methylnaphthalene	91-57-6	10	330
60. Hexachlorocyclopentadiene	77-47-4	10	330
61. 2,4,6-Trichlorophenol	88-06-2	10	330
62. 2,4,5-Trichlorophenol	95-95-4	50	1600
63. 2-Chloronaphthalene	91-58-7	10	330
64. 2-Nitroaniline	88-74-4	50	1600
65. Dimethyl phthalate	131-11-3	10	330
66. Acenaphthylene	208-96-8	10	330
67. 2,6-Dinitrotoluene	606-20-2	10	330
68. 3-Nitroaniline	99-09-2	50	1600
69. Acenaphthene	83-32-9	10	330
70. 2,4-Dinitrophenol	51-28-5	50	1600
71. 4-Nitrophenol	100-02-7	50	1600

Table D-2. Analytes Determined by CLP Semivolatiles Analysis Method (Continued)

Analyte	CAS Number	Contract Required Detection Limits[a] Water (ug/L)	Contract Required Detection Limits[a] Low Soil/Sediment[b,c] (ug/kg)
72. Dibenzofuran	132-64-9	10	330
73. 2,4-Dinitrotoluene	121-14-2	10	330
74. Diethylphthalate	84-66-2	10	330
75. 4-Chlorophenyl phenyl ether	7005-72-3	10	330
76. Fluorene	86-73-7	10	330
77. 4-Nitroaniline	100-01-6	50	1600
78. 4,6-Dinitro-2-methylphenol	534-52-1	50	1600
79. N-nitrosodiphenylamine	86-30-6	10	330
80. 4-Bromophenyl phenyl ether	101-55-3	10	330
81. Hexachlorobenzene	118-74-1	10	330
82. Pentachlorophenol	87-86-5	50	1600
83. Phenanthrene	85-01-8	10	330
84. Anthracene	120-12-7	10	330
85. Di-n-butylphthalate	84-74-2	10	330
86. Fluoranthene	206-44-0	10	330
87. Pyrene	129-00-0	10	330
88. Butyl Benzyl phthalate	85-68-7	10	330
89. 3,3'-Dichlorobenzidine	91-94-1	20	660
90. Benzo(a)anthracene	56-55-3	10	330
91. Chrysene	218-01-9	10	330
92. bis(2-ethylhexyl)phthalate	117-81-7	10	330
93. Di-n-octyl phthalate	117-84-0	10	330
94. Benzo(b)fluoranthene	205-99-2	10	330
95. Benzo(k)fluoranthene	207-08-9	10	330
96. Benzo(a)pyrene	50-32-8	10	330
97. Indeno(1,2,3-cd)pyrene	193-39-5	10	330
98. Dibenz(a,h)anthracene	53-70-3	10	330
99. Benzo(g,h,i)perylene	191-24-2	10	330

a. Specific detection limits are highly matrix dependent. The detection limits listed herein are provided for guidance and may not always be achievable.

b. Detection limits listed for soil/sediment are based on wet weight. The detection limits calculated by the laboratory for soil/sediment, calculated on dry weight basis as required by the contract, will be higher.

c. Contract required detection limits (CRDL) for semivolatiles at medium levels in soil/sediment are 60 times the listed CRDL for semivolatiles at low levels in soil/sediment.

SAMPLE PREPARATION FOR SEMIVOLATILES IN WATER

1.0 SUMMARY OF METHOD

1.1 A measured volume of sample, approximately 1 L, is serially extracted with methylene chloride at a pH greater than 11 and again at a pH less than 2, using a separatory funnel or a continuous extractor. The methylene chloride extracts are dried and concentrated separately to a volume of 1 mL. An extract for pesticide/PCB analysis may be prepared from an aliquot of the extract for semivolatiles, or in a separate extraction procedure. If it is prepared from the semivolatile extract, refer to the procedure for extraction of pesticides/PCBs.

2.0 INTERFERENCES

2.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware, that lead to discrete artifacts and/or elevated baselines in the total ion current profiles (TICPs). All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks. Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source.

3.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

3.1 Samples must be protected from light and refrigerated at 4°C (±2°C) from the time of receipt until analysis or extraction.

3.2 If separatory funnel procedures are employed for extractions for semivolatile analyses, extraction of water samples shall be completed within 5 days of validated time of sample receipts (VTSR). If continuous liquid-liquid extraction procedures are employed, extraction of water samples shall be started within 5 days of VTSR. Extracts must be analyzed within 40 days of VTSR.

4.0 APPARATUS AND EQUIPMENT

4.1 Glassware (brand names and catalog numbers are included for illustration purposes only)

4.1.1 Separatory funnel - 2 L, with Teflon stopcock.

4.1.2 Drying column - 19-mm I.D. chromatographic column with coarse frit. (Substitution of a small pad of Pyrex glass wool for the frit will prevent cross contamination of sample extracts.)

4.1.3 Concentrator tube - Kuderna-Danish, 10 mL, graduated (Kontes K-5700501025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground-glass stopper is used to prevent evaporation of extracts.

4.1.4 Evaporative flask - Kuderna-Danish, 500 mL (Kontes K-5700010500 or equivalent). Attach to concentrator tube with springs.

4.1.5 Snyder column - Kuderna-Danish, three-ball macro (Kontes K-5030000121 or equivalent).

4.1.6 Snyder column - Kuderna-Danish, two-ball micro (Kontes K5690010219 or equivalent).

4.1.7 Vials - Amber glass, 2-mL capacity with Teflon-lined screw cap.

4.1.8 Continuous liquid-liquid extractors - Equipped with Teflon or glass connnecting joints and stopcocks requiring no lubrication (Hershberg-Wolf Extractor-Ace Glass Company, Vineland, NJ, P/N 6841-10 or equivalent).

4.2 Silicon carbide boiling chips - Approximately 10/40 mesh. Heat to 400°C for 30 min or Soxhlet extract with methylene chloride.

4.3 Water bath - Heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.

4.4 Balance - Analytical, capable of accurately weighing 0.0001 g.

4.5 Nitrogen evaporation device - Equipped with a water bath that can be maintained at 35 to 40°C (N-Evap by Organomation Associates, Inc. South Berlin, MA, or equivalent).

5.0 REAGENTS

5.1 Reagent water - Reagent water is defined as a water in which an interferent is not observed at or above the contract required detection limits (CRDL) of each parameter of interest.

5.2 Sodium hydroxide solution (10 N) - Dissolve 40 g of NaOH in reagent water and dilute to 100 mL.

5.3 Sodium thiosulfate - (ACS) Granular.

5.4 Sulfuric acid solution (1 + 1) - Slowly add 50 mL of H_2SO_4 (sp gr. 1.84) to 50 mL of reagent water.

5.5 Acetone, methanol, methylene chloride - Pesticide quality or equivalent.

5.6 Sodium sulfate - (ACS) Powdered, anhydrous. Purify by heating at 400°C for 4 h in a shallow tray, cool in a desiccator, and store in a glass bottle (Baker anhydrous powder, catalog No. 73898, or equivalent).

5.7 Surrogate Standard Spiking Solution

5.7.1 Surrogate standards are added to all samples and calibration solutions; the compounds specified for this purpose are phenol-d_6, 2,4,6-tribromophenol, 2-fluorophenol, nitrobenzene-d_5, terphenyl-d_{14}, and 2-fluorobiphenyl. Two additional surrogates, one base/neutral and one acid, may be added.

5.7.2 Prepare a surrogate standard spiking solution that contains the base/neutral compounds at a concentration of 100 ug/mL, and the acid compounds at 200 ug/mL. Store the spiking solution at 4°C (±2°C) in a Teflon-sealed container. The solution should be checked frequently for stability. The solution must be replaced after 12 months, or sooner if comparison with quality control check samples indicates a problem.

5.8 Matrix standard spiking solution - Prepare a matrix spiking solution that contains each of the following base/neutral compounds at 100 ug/mL in methanol and the following acid compounds at 200 ug/mL in methanol. Analyze duplicate aliquots of a sample spiked with this matrix spiking solution.

Base/Neutrals	Acids
1,2,4-trichlorobenzene	pentachlorophenol
acenaphthene	phenol
2,4-dinitrotoluene	2-chlorophenol
pyrene	4-chloro-3-methylphenol
N-nitroso-di-n-propylamine	4-nitrophenol
1,4-dichlorobenzene	

6.0 PROCEDURE

6.1 Separatory Funnel Extraction

6.1.1 Samples may be extracted using separatory funnel techniques. If emulsions prevent acceptable solvent recovery with separatory funnel extraction, continuous extraction (Section 6.2) may be used. The separatory funnel extraction scheme described below assumes a sample volume of 1 L.

6.1.2 Using a 1-L graduated cylinder, measure out a 1-L sample aliquot and place it into a 2-L separatory funnel. Pipet 1.0 mL of surrogate standard spiking solution into the separatory funnel and mix well. Check the pH of the sample with wide range pH paper and adjust to pH >11 with 10 N sodium hydroxide. Add 1.0 mL of matrix spiking solution to each of two 1-L portions from the sample selected for spiking.

6.1.3 Add 60 mL of methylene chloride to the separatory funnel and extract the sample by shaking the funnel for 2 min, with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods.

6.1.4 Collect the methylene chloride extract in a 250-mL Erlenmeyer flask. If the emulsion cannot be broken (recovery of less than 80 percent of the methylene chloride, corrected for the water solubility of methylene chloride), transfer the sample, solvent and emulsion into the extraction chamber of a continuous extractor. Proceed as described in Section 6.2.3.

6.1.5 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner. Label the combined extract as the base/neutral fraction.

6.1.6 Adjust the pH of the aqueous phase to less than 2 using sulfuric acid (1 + 1). Serially extract three times with 60-mL aliquots of methylene chloride, as per Section 6.1.3. Collect and combine the extracts in a 250-mL Erlenmeyer flask and label the combined extract as the acid fraction.

6.1.7 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of K-D apparatus, if equivalency is demonstrated for all extractable organics listed in Table D-2.

6.1.8 Transfer the individual base/neutral and acid fractions by pouring extracts through separate drying columns containing about 10 cm of anhydrous granular sodium sulfate, and collect the extracts in separate K-D concentrators. Rinse the Erlenmeyer flasks and columns with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

6.1.9 Add one or two clean boiling chips and attach a three-ball Snyder column to the evaporative flask. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80 to 90°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 to 15 min. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of methylene chloride. A 5-mL syringe is recommended for this operation.

6.1.10 Final Concentration of Extract

Concentrate the extract to 1.0 mL using one of the following techniques.

6.1.10.1 Micro Snyder column concentration - Add another one or two clean boiling chips to the concentrator tube and attach a two-ball micro Snyder column. Pre-wet the Snyder column by adding about 0.5 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80 to 90°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches about 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain for at least 10 min while cooling. Remove the Snyder column and rinse its flask and its lower joint into the concentrator tube with 0.2 mL of methylene chloride. Adjust the final volume to 1.0 mL with methylene chloride. If GC/MS analysis will not be performed immediately, stopper the concentrator tube and store refrigerated. If the extracts will be stored longer than two days, they should be transferred to individual Teflon-sealed screw cap bottles and labeled base/neutral or acid fraction, as appropriate.

6.1.10.2 Nitrogen blowdown concentration - Place the concentrator tube in a warm water bath (35°C) and evaporate the solvent volume to just below 1 mL using a gentle stream of clean, dry nitrogen filtered through a column of activated carbon. Caution: New plastic tubing must not be used between the carbon trap and the sample, as it may introduce interferences. The internal wall of the tube must be rinsed down several times with methylene chloride during the operation and the final volume brought to 1 mL with methylene chloride. During evaporation, the tube solvent level must be kept below the water level of the bath. The extract must never be allowed to become dry.

6.2 Continuous Liquid-Liquid Extraction

6.2.1 Check the pH of the sample with wide-range pH paper and adjust to pH 11 with 10 N sodium hydroxide. Transfer a 1-L sample aliquot to the continuous extractor; using a pipet, add 1 mL of surrogate standard spiking solution and mix well.

6.2.2 Add 500 mL of methylene chloride to the distilling flask. Add sufficient reagent water to ensure proper operation and extract for 18 h. Allow to cool, then detach the boiling flask and dry. Concentrate the extract as discussed in Sections 6.1.7 to 6.1.10. Hold the concentrated extract and label as the base/neutral extract.

6.2.3 Add 500 mL of methylene chloride to a clean distilling fla[illegible] and attach it to the continuous extractor. Carefully adjust the pH of the aqueous phase to less than 2 using sulfuric acid (1 + 1). Extract for 18 h. Dry and concentrate the extract as described in Sections 6.1.7 to 6.1.10. Hold the concentrated extract and label as the acid extract.

If the base/neutral and/or acid extracts cannot be concentrated to a final volume of 1 mL, dilute the more concentrated extract to the final volume of the least concentrated extract.

6.3 The samples extracts are ready for GC/MS analysis. Proceed to GC/MS Analysis of Semivolatiles. If high concentrations are suspected (e.g., highly colored extracts), the optional GC/FID screen is recommended.

MEDIUM LEVEL PREPARATION FOR SCREENING AND ANALYSIS OF SEMIVOLATILES IN SOIL/SEDIMENT

1.0 SCOPE AND APPLICATION

1.1 This procedure is designed for the preparation of sediment/soil samples which may contain organic chemicals at a level greater than 20,000 ug/kg.

1.2 The extracts and sample aliquots prepared using this method are screened by GC/MS or GC/FID, using capillary columns for base/ neutral and acid priority pollutants, and related organic chemicals. The results of these screens will determine whether sufficient quantities of pollutants are present to warrant analysis by low or medium protocol.

1.3 If the screenings indicate no detectable pollutants at the lower limits of quantitation, the sample should be prepared by the low level protocol.

2.0 SUMMARY OF METHOD

2.1 Approximately 1-g portions of sediment/soil are transferred to vials and extracted with methylene chloride. The methylene chloride extract is screened for extractable organics by GC/FID or GC/MS.

2.2 If organic compounds are detected by the screen, the methylene chloride extract is analyzed by GC/MS for extractable organics.

2.3 If no organic compounds are detected by the medium level screen, then a low level sample preparation is required.

3.0 INTERFERENCES

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the total ion current profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks. Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source.

3.2 The procedure is designed to allow quantitation limits for screening purposes as low as 20,000 ug/kg for extractable organics. For analysis purposes, the quantitation limits are 20,000 ug/kg for extractable organics. If peaks are present based on the GC/FID screen, the sample is determined to require a medium level analysis by GC/MS. Some samples may contain high concentrations of chemicals that interfere with the analysis of other components at lower levels; the quantitation limits in those cases may be significantly higher.

3.3 These extraction and preparation procedures were developed for rapid and safe handling of high concentration hazardous waste samples. The design of the methods thus does not stress efficient recoveries or low limits of quantitation of all components. Rather, the procedures were designed to screen at moderate recovery and sufficient sensitivity, a broad spectrum of organic chemicals. The results of the analyses thus may reflect only a minimum of the amount actually present in some samples.

4.0 APPARATUS AND EQUIPMENT

4.1 Glass scintillation vials - 20 mL, with screw cap and Teflon or aluminum foil liner.

4.2 Spatula - Stainless steel or Teflon.

4.3 Balance - Capable of weighing 100 g to the nearest 0.01 g.

4.4 Vials and caps - 2 mL for GC autosampler.

4.5 Pasteur pipets - Disposable; glass wool rinsed with methylene chloride.

4.6 Concentrator tubes - 15 mL.

4.7 Ultrasonic cell disruptor - Heat Systems Ultrasonics, Inc., Model W-385 SONICATOR (475 Watt with pulsing capability, No. 200 1/2-in. tapped disruptor horn, and No. 419 1/8-in. standard tapered MICROTIP probe), or equivalent device with a minimum of 375 Watt output capability. NOTE: To ensure that sufficient energy is transferred to the sample during extraction, the MICROTIP probe must be replaced if the tip begins to erode. Erosion of the tip is evidenced by a rough surface.

4.8 Sonabox - Recommended with above disruptors for decreasing cavitation sound.

4.9 Test tube rack.

4.10 Oven - Drying.

4.11 Desiccator.

4.12 Crucibles - Porcelain.

5.0 REAGENTS

5.1 Sodium sulfate - Anhydrous powdered reagent grade, heated at 400°C for 4 h, cooled in a desiccator, and stored in a glass bottle (Baker anhydrous powder, catalog No. 73898 or equivalent).

5.2 Methylene chloride, methanol, and acetone - Pesticide residue analysis grade or equivalent.

5.3 Surrogate Standard Spiking Solution

5.3.1 The compounds specified are phenol-d_5, 2,4,6-tribromophenol, 2-fluorophenol, nitrobenzene-d_5, terphenyl-d_{14}, and 2-fluorobiphenyl. Prepare a solution containing these compounds for base/neutral surrogates at a concentration of 100 ug/mL, and for acid surrogate standards at a concentration of 200 ug/mL in methanol.

5.3.2 Store the spiking solutions at 4°C (±2°C) in Teflon-sealed containers. The solutions should be checked frequently for stability. These solutions must be replaced after 12 months, or sooner, if comparison with quality control check samples indicates a problem.

5.4 Matrix Standard Spiking Solution

5.4.1 Prepare a spiking solution in methanol that contains the following compounds at a concentration of 100 ug/mL for base/neutrals and 200 ug/mL for acids.

Base/Neutrals	Acids
1,2,4-trichlorobenzene	pentachlorophenol
acenaphthene	phenol
2,4-dinitrotoluene	2-chlorophenol
pyrene	4-chloro-3-methylphenol
N-nitroso-di-n-propylamine	4-nitrophenol
1,4-dichlorobenzene	

5.4.2 Store the spiking solutions at 4°C (+2°C) in Teflon-sealed containers. The solutions should be checked frequently for stability. These solutions must be replaced after 12 months, or sooner, if comparison with quality control check samples indicates a problem.

6.0 PROCEDURE

6.1 Transfer the sample container into a fume hood. Open the sample vial. Decant and discard any water layer and then mix the sample. Transfer approximately 1 g (record weight to the nearest 0.1 g) of sample to a 20-mL vial. Wipe the mouth of the vial with a tissue to remove any sample material. Record the exact weight of sample taken. Cap the vial before proceeding with the next sample to avoid any cross-contamination.

6.2 Immediately after weighing the sample for extraction, weigh 5 to 10 g of the sediment into a tared crucible. Determine the percent moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing. Concentrations of individual analytes will be reported relative to the dry weight of sediment.

$$\text{Percent moisture (\%)} = \frac{\text{Weight of sample (g)} - \text{Weight of dry sample (g)}}{\text{Weight of sample (g)}} \times 100$$

6.3 Add 2.0 g of anhydrous powdered sodium sulfate to the sample in the 20-mL vial from Section 6.1 and mix well.

6.4 Surrogate standards are added to all samples, spikes, and blanks. Add 1.0 mL of surrogate spiking solution to the sample mixture.

6.5 Add 1.0 mL of matrix standard spiking solution to each of two 1-g portions from the sample chosen for spiking.

6.6 Immediately add 9.0 mL of methylene chloride to the sample and disrupt the sample with the 1/8-in. tapered MICROTIP ultrasonic probe for 2 min at output control setting 5. (If using a sonicator other than Model W-385, refer to the manufacturer's instructions for appropriate output settings.) Before extraction, make certain that the sodium sulfate is free flowing and not a consolidated mass. As required, break up large lumps with a clear spatula, or very carefully with the tip of the probe.

6.7 Add 8.0 mL of methylene chloride to the matrix spike samples to achieve a final volume of 10 mL.

6.8 Loosely pack disposable Pasteur pipets with 2- to 3-cm glass wool plugs. Filter the extract through the glass wool and collect 5.0 mL in a concentrator tube.

6.9 Place the concentrator tube in a warm water bath (35°C) and evaporate the solvent volume to below 1 mL using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon). Caution: New plastic tubing must not be used between the carbon trap and the sample, since it may introduce interferences.

The internal wall of the tube must be rinsed down several times with methylene chloride during the operation. During evaporation, the tube solvent level must be kept below the water level of the bath. The extract must never be allowed to become dry. Bring the final volume of the extract to 1.0 mL with methylene chloride.

6.10 Transfer the concentrated extract to an autosampler vial for GC/FID or GC/MS capillary column screening. If the extract is screened, the quantitation limits should be approximately 20,000 ug/kg.

LOW LEVEL PREPARATION FOR SCREENING AND ANALYSIS OF SEMIVOLATILES IN SOIL/SEDIMENT

1.0 SUMMARY OF METHOD

1.1 A 30-g portion of soil sediment is mixed with anhydrous powdered sodium sulfate and extracted with 1:1 methylene chloride/acetone using an ultrasonic probe. If the optional low level screen is used, a portion of this dilute extract is concentrated fivefold and is screened by GC/FID or GC/MS. If peaks are present at greater than 20,000 ug/kg, discard the extract and prepare the sample by the medium level method. If no peaks are present at greater than 20,000 ug/kg, the extract is concentrated. An optional gel permeation column cleanup may be used before analysis.

2.0 INTERFERENCES

2.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the total ion current profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks. Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source.

3.0 APPARATUS AND EQUIPMENT

3.1 Apparatus for Determining Percent Moisture

3.1.1 Oven - Drying.

3.1.2 Desiccator.

3.1.3 Crucibles - Porcelain.

3.2 Pasteur pipets - 1-mL, disposable.

3.3 Ultrasonic cell disruptor - Heat Systems Ultrasonics, Inc. Model 375 SONICATOR (375 watt with pulsing capability, No. 305 1/4-in. tapped high gain "Q" disruptor horn or Model 208 3/4-in. standard tip solid horn), or equivalent device with a minimum of 375 watt output capability. Note: To ensure that sufficient energy is transferred to the sample during extraction, the horn must be replaced if the tip begins to erode. Erosion of the tip is evidenced by a rough surface.

3.4 Beakers - 400 mL.

3.5 Vacuum filtration apparatus.

3.6 Buchner funnel.

3.7 Filter paper - Whatman No. 41 or equivalent.

3.8 Kuderna-Danish (K-D) apparatus.

3.8.1 Concentrator tube - 10 mL, graduated (Kontes K-5700401025 or equivalent).

3.8.2 Evaporative flask - 500 mL (Kontes K-5700010500 or equivalent).

3.8.3 Snyder column - Three-ball macro (Kontes K-5030000121 or equivalent).

3.8.4 Snyder column - Two-ball micro (Kontes K-5690010219 or equivalent).

3.9 Silicon carbide boiling chips - Approximately 10/40 mesh. Heat to 400°C for 30 min or Soxhlet extract with methylene chloride.

3.10 Water bath - Heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.

3.11 Balance - Capable of accurately weighing ±0.01 g.

3.12 Vials and caps - 2 mL for GC autosampler.

3.13 Balance - Analytical, capable of accurately weighing ±0.0001 g.

3.14 Nitrogen evaporation device - Equipped with a water bath that can be maintained at 35 to 40°C (N-Evap by Organomation Associates, Inc., South Berlin, MA, or equivalent).

3.15 Gel permeation chromatography (GPC) cleanup device. Note: GPC cleanup is highly recommended for all extracts for low level soils.

3.15.1 Automated system

3.15.1.1 Gel permeation chromatograph (Analytical Biochemical Labs, Inc. GPC Autoprep 1002, or equivalent) including:

3.15.1.2 25-mm I.D. x 600- to 700-mm glass column packed with 70 g of Bio-Beads SX-3.

3.15.1.3 Syringe - 10 mL with Luerlock fitting.

3.15.1.4 Syringe filter holder and filters - Stainless steel and TFE, Gelman 4310 or equivalent.

3.15.2 Manual system assembled from parts*

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*Wise, R.H., D.F. Bishop, R.T. Williams, and B.M. Austern. "Gel Permeation Chromatography in the GC/MS Analysis of Organics in Sludges" U.S. EPA, Municipal Environmental Research Laboratory - Cincinnati, Ohio 45268.

3.15.2.1 25-mm I.D. x 600- to 700-mm heavy wall glass column packed with 70 g of Bio Beads SX-3.

3.15.2.2 Pump - Altex Scientific, Model No. 1001A, semi-preparative, solvent metering system. Pump capacity = 28 mL/min.

3.15.2.3 Detector - Altex Scientific, Model No. 153, with 254 nm UV source and 8-UL semi-preparative flow-cells (2-mm pathlengths).

3.15.2.4 Microprocessor/controller - Altex Scientific, Model No. 420, Microprocessor System Controller, with extended memory.

3.15.2.5 Injector - Altex Scientific, catalog No. 201-56, sample injection valve, Tefzel, with 10-mL sample loop.

3.15.2.6 Recorder - Linear Instruments, Model No. 385, 10-in. recorder.

3.15.2.7 Effluent Switching Valve - Teflon slider valve, 3-way with 0.060-in. ports.

3.15.2.8 Supplemental Pressure Gauge with connecting Tee - U.S. Gauge, 0 to 200 psi, stainless steel. Installed as a downstream monitoring device between column and detector.

Flow rate was typically 5 mL/min of methylene chloride. Recorder chart speed was 0.50 cm/min.

3.16 Pyrex glass wool.

3.17 Pasteur pipets - Disposable.

4.0 REAGENTS

4.1 Sodium sulfate - Anhydrous powdered reagent grade, heated at 400°C for 4 h, cooled in a desiccator, and stored in a glass bottle (Baker anhydrous powder, catalog No. 73898 or equivalent).

4.2 Methylene chloride, methanol, acetone, isooctane, 2-propanol, and benzene - Pesticide quality or equivalent.

4.3 Reagent water - Reagent water is defined as a water in which an interferent is not observed at or above the CRDL of each parameter of interest.

4.4 GPC calibration solutions

4.4.1 Corn oil - 200 mg/mL in methylene chloride.

4.4.2 Bis(2-ethylhexylphthalate) and pentachlorophenol - 4.0 mg/mL in methylene chloride.

4.5 Sodium sulfite - Reagent grade.

4.6 Surrogate Standard Spiking Solution

4.6.1 Surrogate standards are added to all samples, blanks, matrix spikes, matrix spike duplicates, and calibration solutions; the compounds specified for this purpose are phenol-d_6, 2,4,6-tribromophenol, 2-fluorophenol, nitrobenzene-d_5, terphenyl-d_{14}, and 2-fluorobiphenyl. Two additional surrogates, one base/neutral and one acid may be added.

4.6.2 Prepare a surrogate standard spiking solution at a concentration of 100 ug/mL for base/neutral and 200 ug/mL for acids in methanol. Store the spiking solution at 4°C (±2°C) in a Teflon-sealed container. The solution must be replaced after 12 months, or sooner if comparison with quality control check samples indicates a problem.

4.7 Matrix Standard Spiking Solutions

4.7.1 Prepare a matrix spiking solution that contains each of the following compounds in methanol.

Base/Neutrals (100 ug/mL)	Acids (200 ug/mL)
1,2,4-trichlorobenzene	pentachlorophenol
acenaphthene	phenol
2,4-dinitrotoluene	2-chlorophenol
pyrene	4-chloro-3-methylphenol
N-nitroso-di-n-propylamine	4-nitrophenol
1,4-dichlorobenzene	

4.7.2 Store the spiking solution at 4°C (±2°C) in a Teflon-sealed container. The solution should be checked frequently for stability. The solution must be replaced after 12 months, or sooner if comparison with quality control check samples indicates a problem.

4.7.3 Matrix spikes also serve as duplicates, therefore, add volume specified in Section 5.0 to each of two 30-g portions from one sample chosen for spiking.

5.0 PROCEDURE

5.1 Decant and discard any water layer on a sediment sample. Mix samples thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

5.2 Transfer 50 g of soil/sediment to a 100-mL beaker. Add 50 mL of water and stir for 1 h. Determine pH of sample with glass electrode and pH meter while stirring. Report pH value on appropriate data sheets. If the pH of the soil is greater than 11 or less than 5, contact the Project Manager for instructions on how to handle the sample. Document the instructions. Discard this portion of sample.

5.3 The following steps should be performed rapidly to avoid loss of the more volatile extractables.

5.3.1 Weigh approximately 30 g of sample to the nearest 0.1 g into a 400-mL beaker and add 60 g of anhydrous powdered sodium sulfate. Mix well. The sample should have a sandy texture at this point. Immediately, add 100 mL of 1:1 methylene chloride/acetone to the sample, than add the surrogates according to Section 4.6.1.

5.3.2 Immediately after weighing the sample for extraction, weigh 5 to 10 g of the sediment into a tared crucible. Determine the percent moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing. Concentrations of individual analytes will be reported relative to the dry weight of sediment.

$$\text{Percent moisture} = \frac{\text{Weight of sample (g)} - \text{Weight of dry sample (g)}}{\text{Weight of sample (g)}} \times 100$$

5.3.3 Weigh out two 30-g (record weight to nearest 0.1 g) portions for use as matrix and matrix spike duplicates according to Section 5.3.1. When using GPC cleanup, add 2.0 mL of the base/neutral and acid matrix spiking solutions to each of two portions. When not using GPC cleanup, add 1.0 mL of base/neutral and acid matrix spiking solutions to each of the other two portions.

5.3.4 When using GPC cleanup, add 1.0 mL of base/neutral and acid surrogate standard spiking solution to the sample. When not using GPC cleanup, add 0.5 mL of surrogate standard spiking solution to the sample.

5.4 Place the bottom surface of the tip of the 3/4-in. disruptor horn about 1/2 in. below the surface of the solvent but above the sediment layer.

5.5 Sonicate for 3 min using 3/4-in. disruptor horn with output control knob set at 10 and mode switch on pulse and percent duty cycle knob set at 50 percent. Do not use the MICROTIP probe. (If using a sonicator other than Model W-385, refer to the manufacturer's instructions for appropriate output settings.)

5.6 Decant and filter extracts through Whatman No. 41 filter paper using vacuum filtration or centrifuge and decant extraction solvent.

5.7 Repeat the extraction two more times with two additional 100-mL portions of 1:1 methylene chloride/acetone. Before each extraction, make certain that the sodium sulfate is free flowing and not a consolidated mass. As required, break up large lumps with a clean spatula, or very carefully with the tip of the probe. Decant off the extraction solvent after each sonication. On the final sonication, pour the entire sample into the Buchner funnel and rinse with 1:1 methylene chloride/acetone.

5.8 If the sample is to be screened from the low level method, take 5.0 mL and concentrate to 1.0 mL following Section 5.13.2 or 5.13.3. Note that the sample volume in this case is 5.0 mL not 10.0 mL as given in Section 5.13.2. Screen the extract as per the method "Screening of Semivolatile Organic Extracts." Transfer the remainder of the 1 mL back to the total extract from Section 5.7 after GC/FID or GC/MS screening. (Caution: To minimize sample loss, autosamplers which pre-flush samples through the syringe should not be used.)

5.9 Transfer the extract to a K-D concentrator consisting of a 10-mL concentrator tube and a 500-mL evaporative flask. Other concentration devices or techniques may be used if equivalency is demonstrated for all method parameters.

5.10 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (80 to 90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 to 15 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min, and dilute to 10 mL with methylene chloride.

5.11 If GPC cleanup is not used, proceed to Section 5.13.

5.12 GPC Cleanup of Extract

5.12.1 GPC Setup and Calibration

5.12.1.1 Packing the column - Place 70 g of Bio Beads SX-3 in a 400-mL beaker. Cover the beads with methylene chloride; allow the beads to swell overnight (before packing the columns). Transfer the swelled beads to the column and start pumping solvent through the column, from bottom to top, at 5.0 mL/min. After approximately 1 h, adjust the pressure on the column to 7 to 10 psi and pump an additional 4 h to remove air from the column. Adjust the column pressure periodically as required to maintain 7 to 10 psi.

5.12.1.2 Calibration of the column - Load 5 mL of the corn oil solution into sample loop No. 1 and 5 mL of the phthalate-phenol solution into loop No. 2. Inject the corn oil and collect 10-mL fractions (i.e., change fraction at 2-min intervals) for 36 min. Inject the phthalate-phenol solution and collect 15-mL fractions for 60 min. Determine the corn oil elution pattern by evaporation of each fraction to dryness followed by a gravimetric determination of the residue. Analyze the phthalate-phenol fractions by GC/FID on the DB-5 capillary column, a UV spectrophotometer, or a GC/MS system. Plot the concentration of each component in each fraction versus total eluent volume (or time) from the injection points. Choose a "dump time" which allows >85 percent removal of the corn oil and >85 percent recovery of the bis(2-ethylhexyl)-phthalate. Choose the "collect time" to extend at least 10 min after the elution of pentachlorophenol. Wash the column at least 15 min between samples. Typical parameters selected are dump time, 30 min (150 mL); collect time, 36 min (180 mL); and wash time, 15 min (75 mL). The column can also be calibrated by the use of a 254 mm UV detector in place of gravimetric and GC analyses of fractions. Measure the peak areas at various elution times to determine appropriate fractions.

The SX-3 Bio Beads column may be reused for several months, even if discoloration occurs. System calibration usually remains constant over this period of time if column flowrate remains constant.

5.12.2 Prefilter or load all extracts via the filter holder to avoid particulates that might stop the flow. Load one 5.0-mL aliquot of the extract onto the GPC column. Do not apply excessive pressure when loading the GPC. Purge the sample loading tubing thoroughly with solvent between extracts. After especially dirty extracts, run a GPC blank (methylene chloride) to check for carry-over. Process the extracts using the dump, collect, and wash parameters determined from the calibration and collect the cleaned extracts in 400-mL beakers tightly covered with aluminum foil. The phthalate-phenol calibration solution shall be taken through the cleanup cycle with each set of 23 extracts loaded into the GPC. The recovery for each compound must be >85 percent. This must be determined on a GC/FID, using a DB-5 capillary column, a UV recording spectrophotometer, or a GC/MS system. A copy of the printouts of standard and check solution are required as deliverables with each case. Show percent recovery on the copy.

5.12.3 Concentrate the extract as per Sections 5.9 and 5.10.

5.13 Final Concentration of Extract with Optional Extract Splitting Procedure

If the extract in Section 5.10 is to be used only for semivolatile analysis, it must be concentrated to a volume of 1.0 mL, following the procedure in Section 5.13.2.1.

If the extract in Section 5.10 is to be used for both semivolatile and pesticide/PCB analyses, then it must be split into two portions. In that case, follow the procedure in Section 5.13.1 to obtain the pesticide portion, and follow that with the procedure in Section 5.13.2.2 to obtain the semivolatile portion.

Refer to the methods for analysis of pesticides and PCBs for specific instructions regarding the treatment of extracts for pesticide analysis.

5.13.1 If the same extract is used for both semivolatile and pesticide/PCB analyses to split out the pesticide extract, transfer 0.5 mL of the 10-mL methylene chloride extract from Section 5.10 to a separate concentrator tube. Add 5 mL of hexane and a silicon carbide boiling chip and mix using a vortex mixer. Attach a two-ball micro-Snyder column. Pre-wet the Snyder column by adding 0.5 mL of hexane to the top of the column. Place the K-D apparatus on a hot water bath (80 to 90°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 min. Concentrate the extract to an apparent volume of less than 1 mL. Use Section 5.13.3 t reduce the volume to 0.5 mL. Add 0.5 mL of acetone. The pesticide extract must now be passed through an alumina column to remove the base/neutral and acid surrogates and polar interferences. Proceed to the pesticide/PCB analysis method.

5.13.2 Concentration of the semivolatile extract

5.13.2.1 If the extract in Section 5.10 was not split to obtain a portion for pesticide analysis, reattach the micro Snyder column to the concentrator tube used in Section 5.10 which contains the 10-mL extract and add a fresh silicon carbide boiling chip to the concentrator tube. Pre-wet the Snyder column with 0.5 mL of methylene chloride. Place the K-D apparatus on the hot water bath (80 to 90°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 min. When the apparent volume of the liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain for at least 10 min while cooling. Remove the Snyder column and rinse the lower joint into the concentrator tube with 0.2 mL of methylene chloride. Adjust the final volume to 1.0 mL with methylene chloride. If GPC cleanup was used, this 1.0 mL represents a twofold dilution to account for only half of the extract going through the GPC.

5.13.2.2 If the extract in Section 5.10 was split in Section 5.13.1 to obtain a portion for pesticide analysis, reattach the micro-Snyder column to the concentrator tube used in Section 5.10 which contains the 9.5-mL extract and add a fresh silicon carbide boiling chip to the concentrator tube. Pre-wet the Snyder column with 0.5 mL of methylene chloride. Place the K-D apparatus on the hot water bath (80 to 90°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 min. When the apparent volume of the liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain for at least 10 min while cooling. Remove the Snyder column and rinse the lower joint into the concentrator tube with 0.2 mL of methylene chloride. Adjust the final volume to 0.95 mL with methylene chloride. If GPC cleanup was used, this 0.95 mL represents a twofold dilut to account for only half of the extract going through the GPC.

5.13.3 Nitrogen blowdown technique (taken from ASTM Method D 3086). The following method may be used for final concentration of the semivolatile instead of the procedures in Section 5.13.2. Place the concentrator extract tube in a warm water bath (35°C) and evaporate the solvent volume to below 1 mL using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon). Caution: New plastic tubing must not be used between the carbon trap and the sample, since it may introduce interferences.

The internal wall of the tube must be rinsed down several times with methylene chloride during the operation. During evaporation, the tube solvent level must be kept below the water level of the bath. The extract must never be allowed to become dry.

If the extract in Section 5.10 was not split for both semivolatile and pesticide analyses, bring the final volume of the extract to 1.0 mL with methylene chloride. This represents a tenfold concentration. If the extract in Section 5.10 was split in Section 5.13.1, then bring the final volume of the semivolatile portion to 0.95 mL with methylene chloride. This represents a similar tenfold concentration. In either case, if GPC cleanup techniques were employed, the final volume (1.0 or 0.95 mL) represents a twofold dilution to account for the fact that only half the extract went through the GPC.

Store all extracts at 4°C (±2°C) in the dark in Teflon-sealed containers until all analyses are performe

SCREENING OF SEMIVOLATILE ORGANIC EXTRACTS

1.0 SUMMARY OF METHOD

1.1 The solvent extracts of water and sediment/soil are screened on a gas chromatograph/flame ionization detector (GC/FID) using a fused silica capillary column. The results of the screen will determine the concentration of extract taken for GC/MS analysis.

2.0 APPARATUS AND MATERIALS

2.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases. The injection port must be designed for on-column injection when using packed columns, and for splitless injection when using capillary columns.

2.1.1 Flame ionization detector.

2.1.2 GC column - 30 m x 0.32 mm, 1-u film thickness, silicone coated, fused silica capillary column (J & W Scientific DB-5 or equivalent).

3.0 REAGENTS

3.1 Methylene chloride - Pesticide residue analysis grade or equivalent.

3.2 GC calibration standard - Prepare a standard solution containing phenol, phenanthrene, and di-n-octylphthalate.

3.2.1 Stock standard solutions (1.00 ug/uL) - Stock standard solutions can be prepared from pure standard materials or purchased solutions.

3.2.1.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissol the material in pesticide-quality methylene chloride and dilute to volume in a 10-mL volumetric flask. Larger volumes may be used at the convenience of the analyst. If compound purity is assayed at 96 percent or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source and are traceable to standards supplied by EPA's Environmental Monitoring Systems Laboratory in Las Vegas (EMSL-LV).

3.2.1.2 Transfer the stock standard solutions into Teflon-sealed, screw-cap bottles. Store at -10 to -20°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Stock standard solutions must be replaced after 6 months or sooner if comparison with quality control check samples indicates a problem. Standards prepared from gases or reactive compounds such as styrene must be replaced after 2 months, or sooner if comparison with quality control check samples indicates a problem.

3.2.2 Prepare a working standard mixture of the three compounds in methylene chloride. The concentration must be such that the volume injected equals 50 ng of each compound. The storage and stability requirements are the same as specified in Section 3.2.1.2.

4.0 CALIBRATION

4.1 At the beginning of each 12-h shift, inject the GC calibration standard. The following criteria must be

4.1.1 Standardized for half-scale response from 50 ng of phenanthrene

4.1.2 Adequately separated phenol from the solvent front.

4.1.3 Minimum of quarter-scale response for 50 ng of di-n-octylphthalate.

5.0 PROCEDURE

5.1 The suggested GC operating conditions for the screening are:

Initial column temperature hold - 50°C for 4 min
Column temperature program - 50 to 280°C at 8°C/min
Final column temperature hold - 280°C for 8 min
Injector - Grob-type, splitless
Sample volume - 1 to 2 uL
Carrier gas - Helium at 30 cm^3/s.

5.2 Inject the GC calibration standard and ensure the criteria specified in Section 4.0 are met before injecting samples. Estimate the response for 10 ng of phenanthrene.

5.3 Inject the prepared extracts.

5.4 Interpretation of Chromatograms

5.4.1 Water Samples

5.4.1.1 If no sample peaks are detected, or all are less than full-scale deflection, the undiluted extract is analyzed on GC/MS.

5.4.1.2 If any sample peaks are greater than full-scale deflection, calculate the dilution necessary to reduce the major peaks to between half- and full-scale deflection. Use this dilution factor to dilute the extract for GC/MS analysis.

5.4.2 Soil/Sediment Samples

5.4.2.1 If no sample peaks from the extract (from low or medium level preparation) are detected, or all are less than 10 percent full-scale deflection, the sample must be prepared by the low level protocol.

5.4.2.2 Peaks are detected at greater than 10 percent full-scale deflection and less than or equal to full-scale deflection.

5.4.2.2.1 If the screen is from the medium level extract, proceed with GC/MS analysis of this extract with appropriate dilution if necessary.

5.4.2.2.2 If screen is from the low level extract, discard extract and prepare sample by medium level method for GC/MS analysis.

5.4.2.3 Peaks are detected at greater than full-scale deflection.

5.4.2.3.1 If the screen is from the medium level preparation, calculate the dilution necessary to reduce the major peaks to between half- and full-scale deflection. Use this dilution factor to dilute the extract. This dilution is analyzed by GC/MS for extractable organics.

5.4.2.3.2 If the screen is from the low level preparation, discard the extract and prepare a sample by the medium level method for GC/MS analysis.

5.5 Use the information from Section 5.4 to perform the GC/MS analysis of semivolatiles.

GC/MS ANALYSIS OF SEMIVOLATILES

1.0 SUMMARY OF METHOD

1.1 This method is to be used for the GC/MS analysis of semivolatiles screened by the method "Screening of Semivolatile Organic Extracts" and for confirmation of pesticides/PCBs identified by GC/EC, if concentrations permit.

2.0 APPARATUS AND EQUIPMENT

2.1 Gas Chromatograph/Mass Spectrometer System

2.1.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories including syringes, analytical columns, and gases.

2.1.2 Column - 30 m x 0.25 mm I.D. (or 0.32 mm) bonded-phase silicone coated fused silica capillary column (J&W Scientific DB-5 or equivalent). A film thickness of 1.0 u is recommended because of its larger capacity. A film thickness of 0.25 u may be used.

2.1.3 Mass spectrometer - Capable of scanning from 35 to 500 amu every 1 s or less, utilizing 70 V (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all required criteria when 50 ng of decafluorotriphenylphosphine (DFTPP) is injected through the GC inlet. Note: DFTPP criteria must be met before any sample extracts are analyzed. Any samples analyzed when DFTPP criteria have not been met will require re-analysis.

2.1.4 Data system - A computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specific mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an extracted ion current profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits.

3.0 REAGENTS

3.1 Internal standards - 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, perylene-d_{12}. An internal standard solution can be prepared by dissolving 200 mg of each compound in 50 mL of methylene chloride. It may be necessary to use 5 to 10 percent benzene or toluene in this solution and a few minutes of ultrasonic mixing to dissolve all the constituents. The resulting solution will contain each standard at a concentration of 4000 ng/uL. A 10-uL portion of this solution should be added to each 1 mL of sample extract. This will give a concentration of 40 ng/uL of each constituent.

3.2 Prepare calibration standards at a minimum of five concentration levels. Each calibration standard should contain each compound of interest and each surrogate standard. See Section 7.2.1 for calibration standard concentrations. Great care must be taken to maintain the integrity of all standard solutions. Store all standard solutions at -10 to -20°C in screw-cap amber bottles with Teflon liners. Fresh standards should be prepared every 12 months at a minimum. The continuing calibration standard should be prepared weekly and stored at 4°C (±2°C).

4.0 CALIBRATION

4.1 Each GC/MS system must have the hardware tuned to meet the criteria listed in Section 7.1 for a 50-ng injection of DFTPP. No sample analyses can begin until all these criteria are met. These criteria must be demonstrated each 12-h shift. DFTPP has to be injected to meet these criteria. Post-acquisition manipulation of abundances is not acceptable.

4.2 The internal standards selected in Section 3.1 should permit most components of interest in a chromatogram to have retention times of 0.80 to 1.20 relative to the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantification, found in Section 7.1. If interferences are noted, use the next most intense ion as the secondary ion; i.e., for 1,4-dichlorobenzene-d_4, use m/z 152 for quantification.

4.2.1 The internal standards are added to all calibration standards and all sample extracts just prior to analysis by GC/MS. A 10-uL aliquot of the internal standard solution should be added to a 1-mL aliquot of calibration standards.

4.3 Analyze 1 uL of each calibration standard and tabulate the area of the primary characteristic ion against concentration for each compound including the surrogate compounds. Calculate relative response factors (RRF) for each compound using the following equation:

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$

where:

A_x = Area of the characteristic ion for the compound to be measured

A_{is} = Area of the characteristic ion for the specific internal standard

C_{is} = Concentration of the internal standard (ng/uL)

C_x = Concentration of the compound to be measured (ng/uL).

4.3.1 The average relative response factor (RRF) should be calculated for all compounds. A system performance check must be made before this calibration curve is used. Four system performance check compounds (SPCC) are checked for a minimum average relative response factor. The SPCC are N-nitroso-di-n-propylamine, hexachlorocyclopentadiene, 2,4-dinitrophenol, 4-nitrophenol.

4.3.2 A percent relative standard deviation (%RSD) is calculated for eleven compounds labeled the calibration check compounds (CCC) on Form VI (Figures 1 and 2). A maximum %RSD is also specified for these compounds. These criteria must be met for the calibration curve to be valid.

4.4 A check of the calibration curve must be performed once every 12 h during analysis. The minimum relative response factor for the system performance check compounds must be checked. If this criterion is met, the relative response factors of all compounds are calculated. A percent difference of the daily (12 h) relative response factor compared to the average relative response factor from the initial curve is calculated. A maximum percent difference is allowed for each CCC on Form VII (Figures 3 and 4). Only after both these criteria are met can sample analysis begin.

4.5 Internal standard responses and retention times in all standards must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 30 s from the latest daily (12 h) calibration standard, the chromatographic system must be inspected for malfunctions, and corrections made as required. The EICP of the internal standards must be monitored and evaluated for each standard. If EICP area for any internal standard changes by more than a factor of two (-50 to +100 percent), the mass spectrometric system must be inspected for malfunction and corrections made as appropriate. When corrections are made, re-analysis of samples analyzed while the system was malfunctioning is necessary.

5.0 PROCEDURE

5.1 Operating Conditions

5.1.1 The following instrumental parameters for the mass spectrometer are required for all performance tests and for all sample analyses:

Electron energy - 70 V (nominal)
Mass range - 35 to 500 amu
Scan time - not to exceed 1 s/scan.

5.1.2 The recommended GC operating conditions to be used are as follows:

Initial column temperature hold - 40°C for 4 min
Column temperature program - 40 to 270°C at 10°C/min
Final column temperature hold - 270°C for 10 min
Injector temperature - 250 to 300°C
Transfer line temperature - 250 to 300°C
Source temperature - according to manufacturer's specifications
Injector - Grob-type, splitless
Sample volume - 1 to 2 uL
Carrier gas - Helium at 30 cm^3/s

5.2 Combine 0.5 mL of the base/neutral extract and 0.5 mL of the acid extract from the water extract prior to analysis.

5.3 Internal standard solution is added to each sample extract. For water and/or medium soil extracts, add 10 uL of internal standard solution to each accurately measured 1.0 mL of sample extract. If the low soil extracts required a pesticide split, add 9.5 uL of internal standard solution to each accurately measured 0.95 mL of sample extract.

5.4 Analyze the 1.0-mL extract by GC/MS using a bonded-phase silicone-coated fused silica capillary column. Note: Make any extract dilution indicated by characterization prior to the addition of internal standards. If any further dilutions of water or soil/sediment extracts are made, additional internal standards must be added to maintain the required 40 ng/uL of each constituent in the extract volume. If the concentration of any compound exceeds the initial calibration range, the extract must be diluted and re-analyzed. Secondary ion quantitation is only allowed when there are sample interferences with the primary ion. If secondary ion quantitation is performed, document the reasons.

5.5 Qualitative Analysis

5.5.1 The method parameters shall be identified by an analyst competent in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to verify the identifications: (1) elution of the sample component at the GC relative retention time as the standard component, and (2) correspondence of the sample component and standard component mass spectra.

5.5.1.1 For establishing correspondence of the GC relative retention time (RRT), the sample component RRT must compare within ±0.06 RRT units of the RRT of the standard component. For reference, the standard must be run on the same shift as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

5.5.1.2 For comparison of standard and sample component mass spectra, mass spectra obtained on the contractor's GC/MS are required. Once obtained, these standard spectra may be used for identification purposes only if the GC/MS meets the DFTPP daily tuning requirements. These standard spectra may be obtained from the run used to obtain reference RRTs.

5.5.1.3 The requirements for qualitative verification by comparison of mass spectra are as follows:

1. All ions present in the standard mass spectra at a relative intensity greater than 10 percent (most abundant ion in the spectrum equals 100 percent) must be present in the sample spectrum.

2. The relative intensities of ions specified in (1) must agree within ±20 percent between the standard and sample spectra. (Example: For an ion with an abundance of 50 percent in the standard spectra, the corresponding sample ion abundance must be between 30 and 70 percent.)

3. Ions greater than 10 percent in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. The verification process should favor false positives. All compounds meeting the identification criteria must be reported with their spectra. For all compounds below the contract required detection limit (CRDL), report the actual value followed by "J"; e.g., "3J".

5.5.1.4 If a compound cannot be verified by all of the criteria in Section 5.5.1.3, but in the technical judgment of the mass spectral interpretation specialist, the identification is correct, then that identification will be reported and quantification proceeded per Section 6.0.

5.5.2 A library search shall be executed for non-method parameters for the purpose of tentative identification. For this purpose, the 1985 release of the National Bureau of Standards (NBS) Mass Spectral Library (or more recent release), containing 42,261 spectra, shall be used.

5.5.2.1 Up to 20 non-method parameters of greatest apparent concentration for the combined base/neutral/acid fraction shall be tentatively identified via a forward search of the NBS mass spectral library. (Substances with responses less than 10 percent of the nearest internal standard are not required to be searched in this fashion.) Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Note: Computer-generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

5.5.2.2 Guidelines for making tentative identification

1. Relative intensities of major ions in the reference spectrum (ions greater than 10 percent of the most abundant ion) should be present in the sample spectrum.

2. The relative intensities of the major ions should agree within ±20 percent. (Example: For an ion with an abundance of 50 percent in the standard spectra, the corresponding sample ion abundance must be between 30 and 70 percent).

3. Molecular ions present in reference spectrum should be present in sample spectrum.

4. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co-eluting compounds.

5. Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or co-eluting compounds. Note: Data system library reduction programs can sometimes create these discrepancies.

5.5.2.3 If in the technical judgment of the mass interpretation spectral specialist, no valid tentative identification can be made, the compound should be reported as unknown. The mass spectral specialist should give additional classification of the unknown compound, if possible (i.e., unknown phthalate, unknown hydrocarbon, unknown acid type, unknown chlorinated compound). If probable molecular weights can be distinguished, include them.

6.0 CALCULATIONS

6.1 Method parameters identified shall be quantified by the internal standard method. The internal standard used shall be the one nearest the retention time to that of a given analyte. The EICP area of characteristic ions of analytes listed in Tables 1, 2, and 3 is used.

Internal standard responses and retention times in all samples must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 30 s from the latest daily (12 h) calibration standard, the chromatographic system must be inspected for malfunctions, and corrections made as required. The EICP of the internal standards must be monitored and evaluated for each sample, blank, matrix spike, and matrix spike duplicate. If the EICP area for any internal standard changes by more than a factor of two (-50 to +100 percent), the mass spectrometric system must be inspected for malfunction and corrections made as appropriate. If the analysis of a subsequent sample or standard indicates that the system is functioning properly, corrections may not be required. The samples or standards with EICP areas outside the limits must be re-analyzed, and treated according to Sections 6.1.1 and 6.1.2 below. If corrections are made, the laboratory must demonstrate that the mass spectrometric system is functioning properly. This must be accomplished by the analysis of a standard or sample that does meet the EICP criteria. After corrections are made, re-analysis of samples analyzed while the system was malfunctioning is required.

Table 1. Characteristic Ions for Semivolatile Method Parameters

Parameter	Primary Ion	Secondary Ion(s)
Phenol	94	65, 66
bis(-2-Chloroethyl)ether	93	63, 95
2-Chlorophenol	128	64, 130
1,3-Dichlorobenzene	146	148, 113
1,4-Dichlorobenzene	146	148, 113
Benzyl alcohol	108	79, 77
1,2-Dichlorobenzene	146	148, 113
2-Methylphenol	108	107
bis(2-Chloroisopropyl)ether	45	77, 79
4-Methylphenol	108	107
N-Nitroso-di-propylamine	70	42, 101, 130
Hexachloroethane	117	201, 199
Nitrobenzene	77	123, 65
Isophorone	82	95, 138
2-Nitrophenol	139	65, 109
2,4-Dimethylphenol	107	121, 122
Benzoic acid	122	105, 77
bis(-2-Chloroethoxy)methane	93	95, 123
2,4-Dichlorophenol	162	164, 98
1,2,4-Trichlorobenzene	180	182, 145
Naphthalene	128	129, 127
4-Chloroaniline	127	129
Hexachlorobutadiene	225	223, 227
4-Chloro-3-methylphenol	107	144, 142
2-Methylnaphthalene	142	141
Hexachlorocyclopentadiene	237	235, 272
2,4,6-Trichlorophenol	196	198, 200
2,4,5-Trichlorophenol	196	198, 200
2-Chloronaphthalene	162	164, 127
2-Nitroaniline	65	92, 138
Dimethyl phthalate	163	194, 164
Acenaphthylene	152	151, 153
3-Nitroaniline	138	108, 92
Acenaphthene	153	152, 154
2,4-Dinitrophenol	184	63, 154
4-Nitrophenol	109	139, 65
Dibenzofuran	168	139
2,4-Dinitrotoluene	165	63, 182
2,6-Dinitrotoluene	165	89, 121
Diethylphthalate	149	177, 150
4-Chlorophenyl-phenylether	204	206, 141
Fluorene	166	165, 167
4-Nitroaniline	138	92, 108
4,6-Dinitro-2-methylphenol	198	182, 77
N-Nitrosodiphenylamine	169	168, 167
4-Bromophenyl-phenylether	248	250, 141
Hexachlorobenzene	284	142, 249
Pentachlorophenol	266	264, 268
Phenanthrene	178	179, 176

Table 1. Characteristic Ions for Semivolatile Method Parameters (Continued)

Parameter	Primary Ion	Secondary Ion(s)
Anthracene	178	179, 176
Di-n-butylphthalate	149	150, 104
Fluoranthene	202	101, 100
Pyrene	202	101, 100
Butylbenzylphthalate	149	91, 206
3,3'-Dichlorobenzidine	252	254, 126
Benzo(a)anthracene	228	229, 226
bis(2-Ethylhexyl)phthalate	149	167, 279
Chrysene	228	226, 229
Di-n-octyl phthalate	149	-
Benzo(b)fluoranthene	252	253, 125
Benzo(k)fluoranthene	252	253, 125
Benzo(a)pyrene	252	253, 125
Indeno(1,2,3-cd)pyrene	276	138, 227
Dibenz(a, h)anthracene	278	139, 279
Benzo(g, h, i)perylene	276	138, 277

Table 2. Characteristic Ions for Pesticides/PCBs

Parameter	Primary Ion	Secondary Ion(s)
Alpha-BHC	183	181, 109
Beta-BHC	181	183, 109
Delta-BHC	183	181, 109
Gamma-BHC (Lindane)	183	181, 109
Heptachlor	100	272, 274
Aldrin	66	263, 220
Heptachlor epoxide	353	355, 351
Endosulfan I	195	339, 341
Dieldrin	79	263, 279
4,4'-DDE	246	248, 176
Endrin	263	82, 81
Endosulfan II	337	339, 341
4,4'-DDD	235	237, 165
Endosulfan sulfate	272	387, 422
4,4'-DDT	235	237, 165
Methoxychlor	227	228
Chlordane (alpha and/or gamma)	373	375, 377
Toxaphene	159	231, 233
Arochlor-1016	222	260, 292
Arochlor-1221	190	222, 260
Arochlor-1232	190	222, 260
Arochlor-1242	222	256, 292
Arochlor-1248	292	362, 326
Arochlor-1254	292	362, 326
Arochlor-1260	360	362, 394
Endrin ketone	317	67, 319

Table 3. Characteristic Ions for Surrogates and Internal Standards for Semivolatile Compounds

Compound	Primary Ion	Secondary Ion(s)
SURROGATES		
Phenol-d_5	99	42, 71
2-Fluorophenol	112	64
2,4,6-Tribromophenol	330	332, 141
d-5 Nitrobenzene	82	128, 54
2-Fluorobiphenyl	172	171
Terphenyl	244	122, 212
INTERNAL STANDARDS		
1,4-Dichlorobenzene-d_4	152	115
Naphthalene-d_8	136	68
Acenaphthene-d_{10}	164	162, 160
Phenanthrene-d_{10}	188	94, 80
Chrysene-d_{12}	240	120, 236
Perylene-d_{12}	264	260, 265

6.1.1 If, after re-analysis, the EICP areas for all internal standards are inside the contract limits (-50 to +100 percent), the problem with the first analysis is considered to have been within the control of the laboratory. Therefore, only submit data from the analysis with EICP within the contract limits. This is considered the initial analysis and must be reported as such on all data deliverables.

6.1.2 If the re-analysis of the sample does not solve the problem (i.e., the EICP areas are outside the contract limits for both analyses), submit the EICP data and sample data from both analyses. Distinguish between the initial analysis and the re-analysis on all data deliverables. Document all inspection and corrective actions taken.

6.2 The RRF from the daily standard analysis is used to calculate the concentration in the sample. Secondary ions may be used if interferences are present. The area of a secondary ion cannot be substituted for the area of a primary ion unless a relative response factor is calculated using the secondary ion. When method parameters are below CRDL but the spectra meet the identification criteria, report the concentration with a "J". For example, if CRDL is 10 ug/L and concentration of 3 ug/L is calculated, report as "3J".

6.2.1 Calculate the concentration in the sample using the RRF as determined in Section 4.3 and the following equation:

Water

$$\text{Concentration (ug/L)} = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RRF)(V_o)(V_i)}$$

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where:

A_x = Area of the characteristic ion for the compound to be measured

A_{is} = Area of the characteristic ion for the internal standard

I_s = Amount of internal standard injected (ng)

V_o = Volume of water extracted (mL)

V_i = Volume of extract injected (uL)

V_t = Volume of total extract. (Use 2000 uL or a factor of this when dilutions are made. The 2000 uL is derived from combining half of the 1-mL base/neutral extract and half of the 1-mL acid extract.)

Soil/Sediment

$$\begin{array}{l}\text{Concentration (ug/kg)} \\ \text{(Dry weight basis)}\end{array} = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RRF)(V_i)(W_s)(D)}$$

where:

A_x, I_s, A_{is} = Same as given for water (above)

V_t = Volume of low level total extract. (Use 1000 uL or a factor of this when dilutions are made. If GPC cleanup is used, the volume is 2000 uL. The 1000 uL is derived from concentrating the 9.5-mL extract to 0.95 mL.)

- or -

V_t = Volume of medium level extract. (Use 2000 uL or a factor of this when dilutions are made. The 2000 uL is derived from concentrating 5 mL of the 10-mL extract to 1 mL.)

V_i = Volume of extract injected (uL)

$D = \frac{100 - \text{percent moisture}}{100}$

W_s = Weight of sample extracted (g).

6.3 An estimated concentration for non-method parameters tentatively identified shall be quantified by the internal standard method. For quantification, the nearest internal standard free of interferences shall be used.

6.3.1 The formula for calculating concentrations is the same as in Section 6.2.1. Total area counts (or peak heights) from the total ion chromatograms are to be used for both the compound to be measured and the internal standard. An RRF of one (1) is to be assumed. The value from this quantitation shall be qualified as estimated. This estimated concentration should be calculated for all tentatively identified compounds as well as those identified as unknowns.

6.4 Calculate surrogate standard recovery on all samples, blanks and spikes. Determine if recovery is within limits and report on appropriate form.

6.4.1 If recovery is not within limits (i.e., if two surrogates from either base/neutral or acid fractions are out of limits or if recovery of any one surrogate in either fraction is below 10 percent), the following is required:

1. Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.

2. Re-analyze the sample if none of the above reveals a problem.

6.4.2 If the re-analysis of the sample solves the problem, then the problem was within the laboratory's control. Therefore, only submit data from the analysis with surrogate spike recoveries within the contract windows. This shall be considered the initial analysis and shall be reported as such on all data deliverables.

6.4.3 If none of the steps in Section 6.4.1 or 6.4.2 solve the problem, re-extract and re-analyze the sample. If the re-extraction and re-analysis of the sample solves the problem, the problem was within the laboratory's control. Therefore, only submit data from the analysis with surrogate spike recoveries within the contract windows. This shall be considered the initial analysis and shall be reported as such on all data deliverables.

6.4.4 If the re-extraction and re-analysis of the sample does not solve the problem (i.e., the surrogate recoveries are outside the contract limits for both analyses), submit the surrogate spike recovery data and the sample analysis data from analysis of both sample extracts. Distinguish between the initial analysis and the re-analysis on all data deliverables.

6.4.5 If the sample with surrogate recoveries outside the limits is the sample used for the matrix spike and matrix spike duplicate and the surrogate recoveries of the matrix spike and matrix spike duplicate show the same pattern (i.e., outside the limits), the sample, matrix spike, and matrix spike duplicate do not require re-analysis. Document the similarity in surrogate recoveries.

7.0 QUALITY ASSURANCE/QUALITY CONTROL

7.1 Tuning and GC/MS Mass Calibration

It is necessary to establish that a given GC/MS meets the standard mass spectral abundance criteria prior to initating any on-going data collection. This is accomplished through the analysis of DFTPP.

Definition: The 12-h time period for GC/MS system tuning and standards calibration (initial or continuing calibration criteria) begins at the moment of injection of the DFTPP analysis that the laboratory submits as documentation of a compliant tune. The time period ends after 12 h has elapsed according to the system clock.

7.1.1 Each GC/MS system used for the analysis of semivolatile or pesticide compounds must be hardware tuned to meet the abundance criteria listed in Table 4 for a 50-ng injection of DFTPP. DFTPP may be analyzed separately or as part of the calibration standard. The criteria must be demonstrated daily or for each 12-h period, whichever is more frequent, before samples can be analyzed. DFTPP must be injected to meet this criterion. If required, background subtraction must be straightforward and designed only to eliminate column bleed or instrument background ions. Background subtraction actions resulting in spectral distortions for the sole purpose of meeting the contract specifications are unacceptable. Note: All instrument conditions must be identical to those used in sample analysis, except that a different temperature program may be used.

7.1.2 Whenever the analyst takes corrective action which may change or affect the tuning criteria for DFTPP (e.g., ion source cleaning or repair, etc.), the tune must be verified irrespective of the 12-h tuning requirements.

Table 4. DFTPP Key Ions and Ion Abundance Criteria

Mass	Ion Abundance Criteria
51	30.0 - 60.0 percent of mass 198
68	less than 2.0 percent of mass 69
70	less than 2.0 percent of mass 69
127	40.0 - 60.0 percent of mass 198
197	less than 1.0 percent of mass 198
198	base peak, 100 percent relative abundance
199	5.0 - 9.0 percent of mass 198
275	10.0 - 30.0 percent of mass 198
365	greater than 1.00 percent of mass 198
441	present but less than mass 443
442	greater than 40.0 percent of mass 198
443	17.0 - 23.0 percent of mass 442

7.1.3 Calibration should be documented in the form of a bar graph spectrum and as a mass listing.

Form V (GC/MS Tuning and Mass Calibration, Figure 5) should be completed each time an analytical system is tuned. In addition, all samples, standards, blanks, matrix spikes, and matrix spike duplicates analyzed during a particular tune must be summarized in chronological order on the bottom of the appropriate Form V. Detailed instructions for the completion of Form V can be found in the CLP Statement of Work for Organics Analysis.

7.2 Initial Calibration of the GC/MS System

Prior to the analysis of samples and required blanks and after tuning criteria have been met, the GC/MS system must be initially calibrated at a minimum of five concentrations to determine the linearity of response using method parameter standards. Once the system has been calibrated, the calibration must be verified each 12-h time period for each GC/MS system.

7.2.1 Prepare calibration standards as described in Section 3.2 containing the semivolatile method parameters at 20, 50, 80, 120, and 160 ng (total). If an analyte saturates at the 160-ng concentration level, and the GC/MS system is calibrated to achieve a detection sensitivity of no less than the CRDL, the analyst must document it on Form VI (Figures 6 and 7) and in the Case Narrative, and attach a quantitation report and RIC. In this instance, the laboratory should calculate the results based on a four-point initial calibration for the specific analyte. The use of a secondary ion for quantitation is only allowed when there are sample interferences with the primary ion. If secondary ion quantitation is performed, document the reasons in the Case Narrative. Nine compounds--benzoic acid, 2,4-dinitrophenol, 2,4,5-trichlorophenol, 2-nitroaniline, 3-nitroaniline, 4-nitroaniline, 4-nitrophenol, 4,6-dinitro-2-methylphenol, and pentachlorophenol--will only require a four-point initial calibration at 50, 80, 120, and 160 ng (total) since detection at less than 50 ng per injection is difficult.

7.2.2 The U.S. EPA plans to develop performance-based criteria for response factor data acquired during this program. To accomplish this goal, the U.S. EPA has specified both the concentration levels for initial calibration and the specific internal standard to be used on a compound-by-compound basis for quantitation (Table 5). Establishment of standard calibration procedures is necessary and deviations by the contractor will not be allowed.

7.2.3 Analyze each calibration standard and tabulate the area of the primary characteristic ion (Table 1) against concentration for each compound including all contract required

Table 5. Semivolatile Internal Standards with Corresponding Method Analytes Assigned for Quantification

1,4-Dichlorobenzene-d_4	Naphthalene-d_8	Acenaphthene-d_{10}	Phenanthrene-d_{10}	Chrysene-d_{12}	Perylene-d_{12}
Phenol bis (2-Chloroethyl) ether 2-Chlorophenol 1,3-Dichlorobenzene 1,4-Dichlorobenzene Benzyl alcohol 1,2-Dichlorobenzene 2-Methylphenol bis (2-Chloroisopropyl) ether 4-Methylphenol N-nitroso-Di-n-propylamine Hexachloroethane 2-Fluorophenol[a] Phenol-d_6[a]	Nitrobenzene Isophorone 2-Nitrophenol 2,4-Dimethylphenol Benzoic acid bis (2-Chloroethyxy) methane 2,4-Dichlorophenol 1,2,4-Trichlorobenzene Naphthalene 4-Chloroaniline Hexachlorobutadiene 4-Chloro-3-methylphenol 2-Methylnaphthalene Nitrobenzene-d_5[a]	Hexachlorocyclopentadiene 2,4,6-Trichlorophenol 2,4,5-Trichlorophenol 2-Chloronaphthalene 2-Nitroaniline Dimethyl phthalate Acenaphthylene 3-Nitroaniline Acenaphthene 2,4-Dinotrophenol 4-Nitrophenol Dibenzofuran 2,4-Dinitrotoluene 2,6-Dinitrotoluene Diethyl phthalate 4-Chlorophenyl-phenyl ether Fluorene 4-Nitroaniline 2-Fluorobiphenyl[a] 2,4,6-Tribromophenol[a]	4,6-Dinitro-2-methylphenol N-nitrosodiphenylamine 1,2-Diphenylhydrazine 4-Bromophenyl phenyl ether Hexachlorobenzene Pentachlorophenol Phenanthrene Anthracene Di-n-butyl phthalate Fluoranthene	Pyrene Butylbenzyl phthalate 3,3'-Dichlorobenzidine Benzo(a)-anthracene bis (2-ethylhexyl) phthalate Chrysene Terphenyl-d_{14}[a]	Di-n-octyl phthalate Benzo(b) fluoranthene Benzo(k) fluoranthene Benzo(a) pyrene Indeno (1,2,3-c) pyrene Dibenz (a,h) anthracene Benzo (g,h,i) perylene

a. Surrogate compound

surrogate compounds. The relative retention times of each compound in each calibration run should agree within 0.06 relative retention time units. Late eluting compounds usually will have much better agreement.

Using Table 5 and the following equation, calculate the RRF for each compound at each concentration level.

$$RRF = \frac{A_x}{A_{is}} \times \frac{C_{is}}{C_x}$$

where:

A_x = Area of the characteristic ion for the compound to be measured

A_{is} = Area of the characteristic ion for the specific internal standards from Table 4 or 5

C_{is} = Concentration of the internal standard (ng/uL)

C_x = Concentration of the compound to be measured (ng/uL).

Using the RRF from the initial calibration, calculate the percent relative standard deviations (%RSD) for compounds labeled on Form VI (Figures 6 and 7) as calibration check compounds (CCC) and shown in Table 6 using the following equation:

$$\%RSD = \frac{SD}{\bar{x}} \times 100$$

where:

SD = Standard deviation of initial response factors (per compound)

$\bar{x}$ = Mean of initial relative response factors (per compound).

SD can be calculated from the following equation.

$$SD = \sqrt{\sum_{i=1}^{N} \frac{(x_i - \bar{x})^2}{N-1}}$$

The %RSD for each individual CCC must be less than or equal to 30.0 percent. These criteria must be met for the initial calibration to be valid.

7.2.4 A system performance check must be performed to ensure that minimum average relative response factors are met before the calibration curve is used.

7.2.4.1 For semivolatiles, the system performance check compounds (SPCCs) are N-nitroso-di-n-propylamine, hexachlorocyclopentadiene, 2,4-dinitrophenol, and 4-nitrophenol. The minimum acceptable average relative response factor (RRF) for these compounds is 0.050. These compounds typically have very low RRFs (0.1 to 0.2) and tend to decrease in response as the chromatographic system begins to deteriorate or the standard material begins to deteriorate. These compounds are usually the first to show poor performance. Therefore, they must meet the minimum requirement when the system is calibrated.

7.2.4.2 The initial calibration is valid only after both the %RSD for CCC and the minimum RRF for SPCC have been met. Only after both these criteria are met can sample analysis begin.

7.2.5 Once the initial calibration is validated, calculate and report the average relative response factor (RRF) and percent relative standard deviation (%RSD) for all method parameters. Complete and submit Form V (Figure 5) and Form VI (Figures 6 and 7) for each instrument used to analyze samples under this protocol. Detailed instructions for completion of these forms can be found in the CLP Statement of Work for Organics Analysis.

7.3 Continuing Calibration of GC/MS System

A calibration standard(s) containing all semivolatile method parameters, including all required surrogates, must be analyzed each 12-h time period during analysis. Compare the relative response factor data from the standards each 12 h with the average relative response factor from the initial calibration for a specific instrument. A system performance check must be made each 12 h. If the SPCC criteria are met, a comparison of relative response factors is made for all compounds. This is the same check that is applied during the initial calibration (Form VI, Figures 6 and 7). If the minimum relative response factors are not met, the system must be evaluated and corrective action must be taken before sample analysis begins.

7.3.1 Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatography system. This check must be met before analysis begins. The minimum relative response factor (RRF) for semivolatile SPCC is 0.050.

7.3.2 After the system performance check is met, CCCs listed in Table 6 are used to check the validity of the initial calibration. Calculate the percent difference using the following equation.

$$\text{Percent difference} = \frac{RRF_I - RRF_c}{RRF_I} \times 100$$

where:

RRF_I = Average response factor from initial calibration

RRF_C = Response factor from current verification check standard.

If the percent difference for any compound is greater than 20 percent, the laboratory should consider this a warning limit. If the percent difference for each CCC is less than or equal to 25.0 percent, the initial calibration is assumed to be valid. If the criteria are not met (>25.0 percent difference), for any one calibration check compound, corrective action must be taken. Problems similar to those listed under SPCC could affect this criteria. If no source of the problem can be determined after corrective action has been taken, a new initial five-point calibration must be generated. These criteria must be met before sample analysis begins.

Table 6. Calibration Check Compounds

Base/Neutral Fraction	Acid Fraction
Acenaphthene	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
N-Nitrosodiphenylamine	Phenol
Di-n-octylphthalate	Pentachlorophenol
Fluoranthene	2,4,6-Trichlorophenol
Benzo(a)pyrene	

7.3.3 The U.S. EPA plans to evaluate the long-term stability of response factors during this program. Standardization among contract laboratories is necessary to reach these long-term goals. Along with contract specified concentrations for initial calibration, the U.S. EPA is requiring specific concentrations for each continuing calibration standard(s).

The concentration for each method parameter in the continuing calibration standard(s) is 50 ng (total) for all compounds.

7.3.4 Complete and submit Form VII (Figures 8 and 9) for each GC/MS system used for each 12-h time period. Calculate and report the relative response factor and percent difference for all compounds. Ensure that the minimum RRF for semivolatile SPCCs is 0.050. The percent difference for each CCC must be less than or equal to 25.0 percent. Additional instructions for completing Form VII can be found in the CLP Statement of Work for Organics Analysis.

7.4 Method Blank Analysis

A method blank is a volume of deionized, distilled laboratory water for water samples, or a purified solid matrix for soil/sediment samples, carried through the entire analytical scheme (extraction, concentration, and analysis). For soil/sediment samples, a solid matrix suitable for semivolatile analyses is available from EPA's Environmental Monitoring Systems Laboratory at Las Vegas (EMSL-LV). The method blank volume or weight must be approximately equal to the sample volumes or sample weights being processed.

7.4.1 For the analysis of semivolatile method parameters, a method blank analysis must be performed once

1. Each Case, or

2. Each 14-calendar-day period during which samples in a Case are received (said period beginning with the receipt of the first sample in that Sample Delivery Group), or

3. Each 20 samples in a Case that are of similar matrix (water or soil) or similar concentration (soil only), or

4. Whenever samples are extracted by the same procedure (separatory funnel, continuous liquid-liquid extraction, or sonication),

whichever is most frequent, on each GC/MS or GC system used to analyze samples.

7.4.2 It is the analyst's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead discrete artifacts and/or elevated baselines in gas chromatograms be minimized.

7.4.3 For the purposes of this protocol, an acceptable laboratory method blank should meet the criteria of Sections 7.4.3.1 and 7.4.3.2.

7.4.3.1 A method blank for semivolatile analysis must contain no greater than five times (5X) the contract required detection limit (Table D-2) of the phthalate esters in the method parameter list.

7.4.3.2 For all other method parameters not listed above, the method blank must contain less than the CRDL of any single method parameter.

7.4.3.3 If a laboratory method blank exceeds these criteria, the analyst must consider the analytical system to be out of control. The source of the contamination must be investigated and appropriate corrective measures must be taken and documented before further sample analysis proceeds. All samples processed with a method blank that is out of control (i.e., contaminated) must be re-extracted and re-analyzed.

7.4.4 Report results of method blank analysis using Form I (Organic Analysis Data Sheet, Figures 1 and 2) and Form I, TIC (Figure 10). In addition, the samples associated with each method blank must be summarized on Form IV (Method Blank Summary, Figure 11). Detailed instructions for the completion of these forms are in the Contract Laboratory Program (CLP) Statement of Work for Organic Analysis. All sample concentration data shall be reported as uncorrected for blanks.

7.5 Surrogate Spike Analysis

Surrogate standard determinations are performed on all samples and blanks. All samples and blanks are fortified with surrogate spiking compounds before purging or extraction in order to monitor preparation and analysis of samples.

7.5.1 Each sample, matrix spike, matrix spike duplicate, and blank is spiked with surrogate compounds prior to extraction. The surrogate spiking compounds shown in Table 7 are used to fortify each sample, matrix spike, matrix spike duplicate, and blank with the proper concentrations. Performance-based criteria are generated from laboratory results. Therefore, deviations from the spiking protocol will not be permitted.

7.5.2 Surrogate spike recovery must be evaluated by determining whether the concentration (measured as percent recovery) falls inside the contract required recovery limits listed in Table 8.

Table 7. Surrogate Spiking Compounds

		Amount in Sample Extract[a]	
Compounds	Fraction	Water	Low/Medium Soil
Nitrobenzene-d_5	BNA	50 ug	50 ug
2-Fluorobiphenyl	BNA	50 ug	50 ug
p-Terphenyl-d_{14}	BNA	50 ug	50 ug
Phenol-d_5	BNA	100 ug	100 ug
2-Fluorophenol	BNA	100 ug	100 ug
2,4,6-Tribromophenol	BNA	100 ug	100 ug

a. At the time of injection, before any optional dilution.

Table 8. Contract Required Surrogate Spike Recovery Limits

Fraction	Surrogate Compound	Water	Low/Medium Soil
BNA	Nitrobenzene-d_5	35-114	23-120
BNA	2-Fluorobiphenyl	43-116	30-115
BNA	p-Terphenyl-d_{14}	33-141	18-137
BNA	Phenol-d_5	10-94	24-113
BNA	2-Fluorophenol	21-100	25-121
BNA	2,4,6-Tribromophenol	10-123	19-122

7.5.3 Method Blank Surrogate Spike Recovery

The laboratory must take the actions listed below if recovery of any one surrogate compound in either the base/neutral or acid fraction is outside of contract surrogate spike recovery limits.

7.5.3.1 Check calculations to ensure that there are no errors; check internal standard and surrogate spiking solutions for degradation, contamination, etc.; also check instrument performance.

7.5.3.2 Re-analyze the blank extract if steps in Section 7.5.3.1 fail to reveal the cause of the noncompliant surrogate recoveries.

7.5.3.3 Re-extract and re-analyze the blank.

7.5.3.4 If the measures listed in Sections 7.5.3.1 and 7.5.3.3 fail to correct the problem, the analytical system must be considered to be out of control. The problem must be corrected before continuing. This may mean recalibrating the instrumentation but it may also mean more extensive action. The specific corrective action is left up to the GC/MS operator. When surrogate recovery(ies) in the blank is (are) outside of the contract required windows, all samples associated with that blank must be re-analyzed.

7.5.4 Sample Surrogate Spike Recovery

The laboratory must take the actions listed below if either of the following conditions exists:

1. Recovery of any one surrogate compound in either base/neutral or acid fraction is below 10 percent

2. Recoveries of two surrogate compounds in either base/neutral or acid fractions are outside surrogate spike recovery limits.

7.5.4.1 The laboratory shall document (in this instance, document means to write down and discuss the problem and corrective action taken) deviations outside of acceptable quality control limits and take the following actions.

7.5.4.1.1 Check calculations to ensure that there are no errors; check internal standard and surrogate spiking solutions for degradation, contamination, etc.; also check instrument performance.

7.5.4.1.2 If the steps in Section 7.5.4.1.1 fail to reveal a problem, re-analyze the extract. If re-analysis of the extract solves the problem, the problem was within the laboratory's control. Therefore, only submit data from the analysis with surrogate spike recoveries within the contract windows. This shall be reported as such on all data deliverables.

7.5.4.1.3 If the steps in Section 7.5.4.1.2 fail to solve the problem, re-extract and re-analyze the sample. If the re-extraction and re-analysis solves the problem, the problem was in the laboratory's control. Therefore, only submit data from the extraction and analysis with surrogate spike recoveries within the contract windows. This shall be considered the initial analysis and shall be reported as such on all data deliverables.

If the re-extraction and re-analysis of the sample does not solve the problem (i.e., surrogate recoveries are outside the contract windows for both analyses), submit the surrogate spike recovery data and the sample data from both analyses according to Section 7.5.5. Distinguish between the initial analysis and the re-analysis on all data deliverables.

7.5.5 Report surrogate recovery data for the following:

1. Method blank analysis

2. Sample analysis

3. Matrix spike/matrix spike duplicate analyses

4. All sample re-analyses that substantiate a matrix effect.

The surrogate spike recovery data are summarized on Form II (Surrogate Spike Percent Recovery Summary, Figures 12 and 13). Detailed instructions for the completion of Form II can be found in the CLP Statement of Work for Organic Analysis.

7.6 Matrix Spike/Matrix Spike Duplicate Analysis

To evaluate the matrix effect of the sample upon the analytical methodology, the matrix spiking solutions listed in Table 9 should be used for matrix spike and matrix spike duplicate analyses. These compounds are subject to change depending upon availability and suitability for use as matrix spikes.

7.6.1 A matrix spike analysis and matrix spike duplicate analysis must be performed for each group of samples of a similar matrix, once:

1. Each Case of field samples received, or

2. Each 20 field samples in a Case, or

3. Each group of samples of a similar concentration level (soils only), or

4. Each 14-calendar-day period during which samples in a Case were received (said period beginning with the receipt of the first sample in that Sample Delivery Group),

whichever is most frequent.

7.6.2 The amount of matrix spiking solution to be added to the sample aliquots prior to extraction is stipulated in the sample prepation methods. Each method allows for optional dilution steps which must be accounted for when calculating percent recovery of the matrix spike and matrix spike duplicate samples.

Samples requiring optional dilutions and chosen as the matrix spike or matrix spike duplicate samples, must be analyzed at the same dilution as the original unspiked sample.

Table 9. Matrix Spiking Solutions

Base/Neutrals	Acids
1,2,4-Trichlorobenzene	Pentachlorophenol
Acenaphthene	Phenol
2,4-Dinitrotoluene	2-Chlorophenol
Pyrene	4-Chloro-3-methylphenol
N-Nitroso-di-n-propylamine	4-Nitrophenol
1,4-Dichlorobenzene	

7.6.3 Individual component recoveries of the matrix spike are calculated using the following equation.

$$\text{Matrix spike percent recovery} = \frac{SSR - SR}{SA} \times 100$$

Where:

SSR = Spike sample results

SR = Sample result

SA = Spike added from spiking mix.

7.6.4 Calculate the relative percent difference (RPD) between the matrix spike and matrix spike duplicate using the following equation.

$$RPD = \frac{|D_1 - D_2|}{(D_1 + D_2)/2} \times 100$$

where:

D_1 = First sample value

D_2 = Second sample value (duplicate).

7.6.5 The matrix spike results (concentrations) for nonspiked method parameters shall be reported on Form I (Organic Analysis Data Sheet, Figures 1 and 2) and the matrix spike percent recoveries shall be summarized on Form III (MS/MSD Recovery, Figures 14 and 15). These values will be used by EPA to periodically update existing performance-based QC recovery limits (Table 10).

The results for nonspiked method parameters in the matrix spike duplicate analysis shall be reported on Form I (Organic Analysis Data Sheet, Figures 1 and 2) and the percent recovery and the relative percent difference shall be summarized on Form III (MS/MSD Recovery, Figures 14 and 15). The RPD data will be used by EPA to evaluate the long-term precision of the analytical method. Detailed instructions for the completion of Form III can be found in the CLP Statement of Work for Organics Analysis.

Table 10. Matrix Spike Recovery Limits

Fraction	Matrix Spike Compound	Water	Soil/Sediment
Base/Neutral	1,2,4-Trichlorobenzene	39-98	38-107
Base/Neutral	Acenaphthene	46-118	31-137
Base/Neutral	2,4-Dinitrotoluene	24-96	28-89
Base/Neutral	Pyrene	26-127	35-142
Base/Neutral	N-Nitroso-di-n-propylamine	41-116	41-126
Base/Neutral	1,4-Dichlorobenzene	36-97	28-104
Acid	Pentachlorophenol	9-103	17-109
Acid	Phenol	12-89	26-90
Acid	2-Chlorophenol	27-123	25-102
Acid	4-Chloro-3-Methylphenol	23-97	26-103
Acid	4-Nitrophenol	10-80	11-114

7.7 Quality Control Activities Involved with Sample Analysis

The intent of Section 7.7 is to provide the analyst with a brief summary of ongoing quality control activities involved with sample analysis. Specific references are provided to help the analyst meet specific reporting and deliverables requirements.

7.7.1 Samples can be analyzed upon successful completion of the initial QC activities. When 12 h have elapsed since the initial tune was completed, it is necessary to conduct an instrument tune and calibration check analysis (Section 7.2). Any major system maintenance, such as a source cleaning or installation of a new column, may necessitate a retune and recalibration. Minor maintenance should necessitate only the calibration verification (Section 7.3).

7.7.2 Internal Standards Evaluation - Internal standard responses and retention times in all samples must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 s, the chromatographic system must be inspected for malfunctions, and corrections made as required. The EICP of the internal standards must be monitored and evaluated for each sample, blank, matrix spike, and matrix spike duplicate. If the EICP area for any internal standard changes by more than a factor of two (-50 to +100 percent), from the latest daily (12-h time period) calibration standard, the mass spectrometric system must be inspected for malfunction, and corrections made as appropriate. Breaking off 1 ft of the column or cleaning the injector sleeve will often improve high end sensitivity for the late eluting compounds; repositioning or repacking the front end of the column will often improve front end column performance. Poor injection technique can also lead to variable internal standard to internal standard ratios. When corrections are made, re-analysis of samples analyzed while the system was malfunctioning is necessary.

7.7.2.1 If after re-analysis, the EICP areas for all internal standards are inside the contract limits (-50 to +100 percent), the problem with the first analysis is considered to have been within the control of the laboratory. Therefore, only submit data from the analysis with EICPs within the contract limits. This is considered the initial analysis and must be reported as such on all data deliverables.

7.7.2.2 If the re-analysis of the sample does not solve the problem (i.e., the EICP areas are outside contract limits for both analyses), submit the EICP data and sample data from both analyses. Distinguish between the initial analysis and the re-analysis o[illegible] all data deliverables. Document all inspection and corrective actions taken.

7.7.3 Each analytical run must also be checked for saturation. The level at which an individual compound will saturate the detection system is a function of the overall system sensitivity and the mass spectral characteristics of that compound. The initial method calibration (Section 7.2) requires that the system should not be saturated for high response compounds at 160 ng for semivolatile method parameters.

7.7.3.1 If any compound in any sample exceeds the initial calibration range, that sample must be diluted, the internal standard concentration re-adjusted, and the sample re-injected, as described in Section 5.4.

Secondary ion quantitation is only allowed when there are sample matrix interferences with the primary ion.

7.7.3.2 If the dilution of the sample causes any compound detected in the first analysis to be undetectable in the second analysis, then the results of both analyses shall be reported on separate Forms I (Figures 1 and 2).

SEMIVOLATILE ORGANICS ANALYSIS DATA SHEET   EPA SAMPLE NO.

____

Lab Name: ____________________ Contract: ____________ ____________
Lab Code: ________ Case No.: _______ SAS No.: ________ SDG No.: ________
Matrix: (soil/water) ________ Lab Sample ID: ____________
Sample wt/vol: ________ (g/mL) ________ Lab File ID: ____________
Level: (low/med) ________ Date Received: ____________
% Moisture: not dec. _____ dec. _____ Date Extracted: ____________
Extraction: (SepF/Cont/Sonc) _____ Date Analyzed: ____________
GPC Cleanup: (Y/N) _____ pH: _____ Dilution Factor: ____________

CAS NO.	COMPOUND	CONCENTRATION UNITS: (ug/L or ug/kg)________	Q
108-95-2	Phenol		
111-44-4	bis (2-Chloroethyl) ether		
95-57-8	2-Chlorophenol		
541-73-1	1,3-Dichlorobenzene		
106-46-7	1,4-Dichlorobenzene		
100-51-6	Benzyl alcohol		
95-50-1	1,2-Dichlorobenzene		
95-48-7	2-Methylphenol		
108-60-1	bis-(2-Chloroisopropyl) ether		
106-44-5	4-Methylphenol		
621-64-7	N-Nitroso-di-n-propylamine		
67-72-1	Hexachloroethane		
98-95-3	Nitrobenzene		
78-59-1	Isophorone		
88-75-5	2-Nitrophenol		
105-67-9	2,4-Dimethylphenol		
65-85-0	Benzoic acid		
111-91-1	bis (2-Chloroethoxy) methane		
120-83-2	2,4-Dichlorophenol		
120-82-1	1,2,4-Trichlorobenzene		
91-20-31	Naphthalene		
106-47-8	4-Chloroaniline		
87-68-3	Hexachlorobutadiene		
59-50-7	4-Chloro-3-methylphenol		
91-57-6	2-Methylnaphthalene		
77-47-4	Hexachlorocyclopentadiene		
88-06-2	2,4,6-Trichlorophenol		
95-95-4	2,4,5-Trichlorophenol		
91-58-7	2-Chloronaphthalene		
88-74-4	2-Nitroaniline		
131-11-3	Dimethylphthalate		
208-96-8	Acenaphthylene		
606-20-2	2,6-Dinitrotoluene		

FORM I SV-1   1/87 Rev.

Figure 1. Semivolatile Organics Analysis Data Sheet

SEMIVOLATILE ORGANICS ANALYSIS DATA SHEET   EPA SAMPLE N

Lab Name: ____________ Contract: ____________ ____________
Lab Code: ________ Case No.: ________ SAS No.: ________ SDG No.: ________
Matrix: (soil/water) ________ Lab Sample ID: ____________
Sample wt/vol: ________ (g/mL) ________ Lab File ID: ____________
Level: (low/med) ________ Date Received: ____________
% Moisture: not dec. _____ dec. _____ Date Extracted: ____________
Extraction: (SepF/Cont/Sonc) _____ Date Analyzed: ____________
GPC Cleanup: (Y/N) _____ pH: _____ Dilution Factor: ____________

CAS NO.	COMPOUND	CONCENTRATION UNITS: (ug/L or ug/kg)__________	Q
99-09-2	3-Nitroaniline		
83-32-9	Acenaphthene		
51-28-5	2,4-Dinitrophenol		
100-02-7	4-Nitrophenol		
132-64-9	Dibenzofuran		
121-14-2	2,4-Dinitrotoluene		
84-66-2	Diethylphthalate		
7005-72-3	4-Chlorophenyl-phenylether		
86-73-7	Fluorene		
100-01-6	4-Nitroaniline		
534-52-1	4,6-Dinitro-2-methylphenol		
86-30-6	N-Nitrosodiphenylamine (1)		
101-55-3	4-Bromophenyl-phenylether		
118-74-1	Hexachlorobenzene		
87-86-5	Pentachlorophenol		
85-01-8	Phenanthrene		
120-12-7	Anthracene		
84-74-2	Di-n-butylphthalate		
206-44-0	Fluoranthene		
129-00-0	Pyrene		
85-68-7	Butylbenzylphthalate		
91-94-1	3,3'-Dichlorobenzidine		
56-55-3	Benzo(a)anthracene		
218-01-9	Chrysene		
117-81-7	bis(2-Ethylhexyl)phthalate		
117-84-0	Di-n-octylphthalate		
205-99-2	Benzo(b)fluoranthene		
207-08-9	Benzo(k)fluoranthene		
50-32-8	Benzo(a)pyrene		
193-39-5	Indeno(1,2,3-cd)pyrene		
53-70-3	Dibenz(a,h)anthracene		
191-24-2	Benzo(g,h,i)perylene		

(1) Cannot be separated from diphenylamine

FORM I SV-2   1/87 Rev.

Figure 2. Semivolatile Organics Analysis Data Sheet, Continued

SEMIVOLATILE INTERNAL STANDARD AREA SUMMARY

Lab Name: ______________________ Contract: ____________ ____________

Lab Code: ________ Case No.: _______ SAS No.: ________ SDG No.: __________

Lab File ID (Standard): _________ Date Analyzed: __________

Instrument ID: _________ Time Analyzed: __________

		IS1 (DCB) AREA#	RT	IS2 (NPT) AREA#	RT	IS3 (ANT) AREA#	RT
	12 HOUR STD						
	UPPER LIMIT						
	LOWER LIMIT						
	EPA SAMPLE NO.						
1.							
2.							
3.							
4.							
5.							
6.							
7.							
8.							
9.							
10.							
11.							
12.							
13.							
14.							
15.							
16.							
17.							
18.							
19.							
20.							
21.							
22.							

IS1 (DCB) = 1,4-Dichlorobenzene-d_4

IS2 (NPT) = Naphthalene-d_8

IS3 (ANT) = Acenaphthene-d_8

UPPER LIMIT = + 100% of internal standard area.

LOWER LIMIT = - 50% of internal standard area.

#Column used to flag internal standard area values with an asterisk

Page ___ of ___ FORM VIII SV-1 1/87 Rev.

Figure 3. Semivolatile Internal Standard Area Summary

SEMIVOLATILE INTERNAL STANDARD AREA SUMMARY

Lab Name: ____________ Contract: ____________ ____________
Lab Code: ________ Case No.: ________ SAS No.: ________ SDG No.: ________
Lab File ID (Standard): ________ Date Analyzed: ____________
Instrument ID: ________ Time Analyzed: ____________

	IS4 (PHN) AREA#	RT	IS5 (CRY) AREA#	RT	IS4 (PRY) AREA#	RT
12 HOUR STD						
UPPER LIMIT						
LOWER LIMIT						
EPA SAMPLE NO.						
1.						
2.						
3.						
4.						
5.						
6.						
7.						
8.						
9.						
10.						
11.						
12.						
13.						
14.						
15.						
16.						
17.						
18.						
19.						
20.						
21.						
22.						

IS4 (PHN) = Phenanthrene-d_{10}
IS5 (CRY) = Chrysene-d_{12}
IS6 (PRY) = Perylene-d_{12}

UPPER LIMIT = + 100% of internal standard area.
LOWER LIMIT = - 50% of internal standard area.

#Column used to flag internal standard area values with an asterisk

Page ___ of ___ FORM VIII SV-2 1/87 Re

Figure 4. Semivolatile Internal Standard Area Summary, Continued

SEMIVOLATILE ORGANIC GC/MS TUNING AND MASS
CALIBRATION - DECAFLUOROTRIPHENYLPHOSPHINE (DFTPP)

Lab Name: ______________ Contract: ______________
Lab Code: ________ Case No.: ________ SAS No.: ________ SDG No.: ________
Lab File ID: ____________ DFTPP Injection Date: ____________
Instrument ID: ____________ DFTPP Injection Time: ____________

m/e	ION ABUNDANCE CRITERIA	% RELATIVE ABUNDANCE
51	30.0 - 60.0% of mass 198	
68	Less than 2.0% of mass 69	( ) 1
69	Mass 69 relative abundance	
70	Less than 2.0% of mass 69	( ) 1
127	40.0 - 60.0% of mass 198	
197	Less than 1.0% of mass 198	
198	Base peak, 100% relative abundance	
199	5.0 to 9.0% of mass 198	
275	10.0 - 30.0% of mass 198	
365	Greater than 1.00% of mass 198	
441	Present, but less than mass 443	
442	Greater than 40.0% of mass 198	
443	17.0 - 23% of mass 442	( ) 2

1-Value is % mass 69 2-Value is % mass 442

THIS TUNE APPLIES TO THE FOLLOWING SAMPLES, MS, MSD, BLANKS, AND STANDARDS

	EPA SAMPLE NO.	LAB SAMPLE ID	LAB FILE ID	DATE ANALYZED	TIME ANALYZED
01					
02					
03					
04					
05					
06					
07					
08					
09					
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					
21					
22					

Page ___ of ___ FORM V SV 1/87 Rev.

Figure 5. Semivolatile GC/MS Tuning and Mass Calibration

SEMIVOLATILE ORGANICS INITIAL CALIBRATION DATA

Lab Name: ____________________ Contract: ____________
Lab Code: ________ Case No.: ______ SAS No.: ______ SDG No.: ______
Instrument ID: __________ Calibration Date(s): ________ ________

Minimum $\overline{\text{RRF}}$ for SPCC(#) is 0.050 Maximum % RSD for CCC(*) is 30.0%

LAB FILE ID: __________ RRF20 = __________ RRF50 = __________
RRF80 = __________ RRF120= __________ RRF160= __________

COMPOUND	RRF20	RRF50	RRF80	RRF120	RRF160	$\overline{\text{RRF}}$	% RSD
Phenol *							*
bis(-2-Chloroethyl)ether							
2-Chlorophenol							
1,3-Dichlorobenzene							
1,4-Dichlorobenzene *							*
Benzyl Alcohol							
1,2-Dichlorobenzene							
2-Methylphenol							
bis(2-chloroisopropyl) ether							
4-Methylphenol							
N-Nitroso-di-n-propylamine #							#
Hexachloroethane							
Nitrobenzene							
Isophorone							
2-Nitrophenol *							
2,4-Dimethylphenol							
Benzoic Acid							
bis(2-Chloroethoxy) methane							
2,4-Dichlorophenol							
1,2,4-Trichlorobenzene							
Naphthalene							
4-Chloroaniline							
Hexachlorobutadiene *							*
4-Chloro-3-methylphenol *							*
2-Methylnaphthalene							
Hexachlorocyclopentadiene #							#
2,4,6-Trichlorophenol *							*
2,4,5-Trichlorophenol							
2-Chloronaphthalene							
2-Nitroaniline							
Dimethyl phthalate							
Acenaphthylene							
2,6-Dinitrotoluene							
3-Nitroaniline							
Acenaphthene *							*
2,4-Dinitrophenol #							#
4-Nitrophenol #							#

FORM VI SV-1 1/87 Re

Figure 6. Semivolatile Organics Initial Calibration Data

SEMIVOLATILE ORGANICS INITIAL CALIBRATION DATA

Lab Name: ____________________ Contract: ____________
Lab Code: ________ Case No.: ________ SAS No.: ________ SDG No.: ________
Instrument ID: __________ Calibration Date(s): __________ __________

Minimum $\overline{RRF}$ for SPCC(#) is 0.050 Maximum % RSD for CCC(*) is 30.0%

LAB FILE ID: __________ RRF20 = __________ RRF50 = __________
RRF80 = __________ RRF120= __________ RRF160= __________

COMPOUND	RRF20	RRF50	RRF80	RRF120	RRF160	$\overline{RRF}$	% RSD
Dibenzofuran							
2,4-Dinitrotoluene							
Diethylphthalate							
4-Chlorophenyl-phenylether							
Fluorene							
4-Nitroaniline							
4,6-Dinitro-2-methylphenol							
N-Nitrosodiphenylamine(1) *							*
4-Bromophenyl-phenylether							
Hexachlorobenzene							
Pentachlorophenol *							*
Phenanthrene							
Anthracene							
Di-n-butylphthalate							
Fluoranthene *							*
Pyrene							
Butylbenzylphthalate							
3,3'-Dichlorobenzidine							
Benzo(a)anthracene							
Chrysene							
bis(2-Ethylhexyl)phthalate							
Di-n-octylphthalate *							*
Benzo(b)fluoranthene							
Benzo(k)fluoranthene							
Benzo(a)pyrene *							*
Indeno(1,2,3-cd)pyrene							
Dibenz(a,h)anthracene							
Benzo(g,h,i)perylene							
Nitrobenzene-d_5							
2-Fluorobiphenyl							
Terphenyl-d_{14}							
Phenol-d_5							
2-Fluorophenol							
2,4,6-Tribromophenol							

(1)Cannot be separated from Diphenylamine

FORM VI SV-2 1/87 Rev.

Figure 7. Semivolatile Organics Initial Calibration Data (Continued)

SEMIVOLATILE CONTINUING CALIBRATION CHECK

Lab Name: ______________________ Contract: ____________
Lab Code: ________ Case No.: ______ SAS No.: ______ SDG No.: ______
Instrument ID: __________ Calibration Date(s): ________ Time: ______
Lab File ID: __________ Init. Calib. Date(s): ________ ______

Minimum RRF50 for SPCC (#) is 0.050 Maximum % D for CCC(*) is 30.0%

COMPOUND	$\overline{RRF}$	RRF50	%D
Phenol	*		*
bis(-2-Chloroethyl)ether			
2-Chlorophenol			
1,3-Dichlorobenzene			
1,4-Dichlorobenzene	*		*
Benzyl alcohol			
1,2-Dichlorobenzene			
2-Methylphenol			
bis(2-chloroisopropyl) ether			
4-Methylphenol			
N-Nitroso-di-n-propylamine	#		#
Hexachloroethane			
Nitrobenzene			
Isophorone			
2-Nitrophenol	*		*
2,4-Dimethylphenol			
Benzoic acid			
bis(2-Chloroethoxy) methane			
2,4-Dichlorophenol			
1,2,4-Trichlorobenzene			
Naphthalene			
4-Chloroaniline			
Hexachlorobutadiene	*		*
4-Chloro-3-methylphenol	*		*
2-Methylnaphthalene			
Hexachlorocyclopentadiene	#		#
2,4,6-Trichlorophenol	*		*
2,4,5-Trichlorophenol			
2-Chloronaphthalene			
2-Nitroaniline			
Dimethyl Phthalate			
Acenaphthylene			
2,6-Dinitrotoluene			
3-Nitroaniline			
Acenaphthene	*		*
2,4-Dinitrophenol	#		#
4-Nitrophenol	#		#

FORM VII SV-1 1/87 Rev

Figure 8. Semivolatile Continuing Calibration Check

SEMIVOLATILE CONTINUING CALIBRATION CHECK

Lab Name: ______________________ Contract: __________
Lab Code: ________ Case No.: ________ SAS No.: ________ SDG No.: ________
Instrument ID: __________ Calibration Date(s): __________ Time: ________
Lab File ID: __________ Init. Calib. Date(s): __________ ________

Minimum RRF50 for SPCC(#) is 0.050 Maximum % D for CCC(*) is 25.0%

COMPOUND	RRF	RRF50	%D
Dibenzofuran			
2,4-Dinitrotoluene			
Diethylphthalate			
4-Chlorophenyl-phenylether			
Fluorene			
4-Nitroaniline			
4,6-Dinitro-2-methylphenol			
N-Nitrosodiphenylamine(1) *			*
4-Bromophenyl-phenylether			
Hexachlorobenzene			
Pentachlorophenol *			*
Phenanthrene			
Anthracene			
Di-n-butylphthalate			
Fluoranthene *			*
Pyrene			
Butylbenzylphthalate			
3,3'-Dichlorobenzidine			
Benzo(a)anthracene			
Chrysene			
bis(2-Ethylhexyl)phthalate			
Di-n-octylphthalate *			*
Benzo(b)fluoranthene			
Benzo(k)fluoranthene			
Benzo(a)pyrene *			*
Indeno(1,2,3-cd)pyrene			
Dibenz(a,h)anthracene			
Benzo(g,h,i)perylene			
Nitrobenzene-d_5			
2-Fluorobiphenyl			
Terphenyl-d_{14}			
Phenol-d_5			
2-Fluorophenol			
2,4,6-Tribromophenol			

(1)Cannot be separated from Diphenylamine

FORM VII SV-2 1/87 Rev.

Figure 9. Semivolatile Continuing Calibration Check (Continued)

SEMIVOLATILE ORGANICS ANALYSIS DATA SHEET
TENTATIVELY IDENTIFIED COMPOUNDS

EPA SAMPLE NO

Lab Name: ____________ Contract: ____________
Lab Code: ________ Case No.: ________ SAS No.: ________ SDG No.: ________
Matrix: (soil/water) ________ Lab Sample ID: ____________
Sample wt/vol: ________ (g/mL) ________ Lab File ID: ____________
Level: (low/med) ________ Date Received: ____________
% Moisture: not dec. ________ dec. ______ Date Extracted: ____________
Extraction: (SepF/Cont/Sonc) ______ Date Analyzed: ____________
GPC Cleanup: (Y/N) ____ pH: ______ Dilution Factor: ____________

Number TICs found: ________

CONCENTRATION UNITS:
(ug/L or ug/kg) ____________

CAS NUMBER	COMPOUND NAME	RT	EST. CONC.	Q
1.				
2.				
3.				
4.				
5.				
6.				
7.				
8.				
9.				
10.				
11.				
12.				
13.				
14.				
15.				
16.				
17.				
18.				
19.				
20.				
21.				
22.				
23.				
24.				
25.				
26.				
27.				
28.				
29.				
30.				

FORM I SV-TIC 1/87 Rev.

Figure 10. Semivolatile Organics Analysis Data Sheet Tentatively Identified Compounds

SEMIVOLATILE METHOD BLANK SUMMARY

Lab Name: ______________________ Contract: ___________

Lab Code: _______ Case No.: ______ SAS No.: ______ SDG No.: ______

Lab File ID: __________ Lab Sample ID: __________

Date Extracted: __________ Extraction: (SepF/Cont/Sonc)_____

Date Analyzed: __________ Time Analyzed: __________

Matrix: (soil/water) ________ Level: (low/med) __________

Instrument ID: __________

THIS METHOD BLANK APPLIES TO THE FOLLOWING SAMPLES, MS AND MSD:

	EPA SAMPLE NO.	LAB SAMPLE ID	LAB FILE ID	DATE ANALYZED
01				
02				
03				
04				
05				
06				
07				
08				
09				
10				
11				
12				
13				
14				
15				
16				
17				
18				
19				
20				
21				
22				
23				
24				
25				
26				
27				
28				
29				
30				

COMMENTS: ____

____

Page ___ of ___ FORM IV SV 1/87 Rev.

Figure 11. Semivolatile Method Blank Summary

WATER SEMIVOLATILE SURROGATE RECOVERY

Lab Name: ______________________ Contract: ____________

Lab Code: ________ Case No.: ______ SAS No.: ______ SDG No.: ______

	EPA SAMPLE NO.	S1 (NBZ)#	S2 (FBP)#	S3 (TPH)#	S4 (PHL)#	S5 (2FP)#	S6 (TBP)#	OTHER	TOT OUT
01									
02									
03									
04									
05									
06									
07									
08									
09									
10									
11									
12									
13									
14									
15									
16									
17									
18									
19									
20									
21									
22									
23									
24									
25									
26									
27									
28									
29									
30									

	QC LIMITS
S1 (NBZ) = Nitrobenzene-d_5	(35-114)
S2 (FBP) = 2-Fluorobiphenyl	(43-116)
S3 (TPH) = Terphenyl-d_{14}	(33-141)
S4 (PHL) = Phenol-d_5	(10-94)
S5 (2FP) = 2-Fluorophenol	(21-100)
S6 (TBP) = 2,4,6-Tribromophenol	(10-123)

#Column to be used to flag recovery values
*Values outside of contract required QC limits
D Surrogates diluted out

Page ___ of ___ FORM II SV-1 1/87 Rev.

Figure 12. Water Semivolatile Surrogate Recovery

SOIL SEMIVOLATILE SURROGATE RECOVERY

Lab Name: ______________________ Contract: ____________
Lab Code: ________ Case No.: ________ SAS No.: ________ SDG No.: ________
Level: (low/med) ______

	EPA SAMPLE NO.	S1 (NBZ)#	S2 (FBP)#	S3 (TPH)#	S4 (PHL)#	S5 (2FP)#	S6 (TBP)#	OTHER	TOT OUT
01									
02									
03									
04									
05									
06									
07									
08									
09									
10									
11									
12									
13									
14									
15									
16									
17									
18									
19									
20									
21									
22									
23									
24									
25									
26									
27									
28									
29									
30									

		QC LIMITS
S1 (NBZ)	= Nitrobenzene-d_5	(23-120)
S2 (FBP)	= 2-Fluorobiphenyl	(30-115)
S3 (DCE)	= Terphenyl-d_{14}	(18-137)
S4 (PHL)	= Phenol-d_5	(24-113)
S5 (2FP)	= 2-Fluorophenol	(25-121)
S6 (TBP)	= 2,4,6-Tribromophenol	(19-122)

#Column to be used to flag recovery values
*Values outside of contract required QC limits
D Surrogates diluted out

Page ___ of___ FORM II SV-2 1/87 Rev.

Figure 13. Soil Semivolatile Surrogate Recovery

WATER SEMIVOLATILE MATRIX SPIKE/MATRIX SPIKE DUPLICATE RECOVERY

Lab Name: ____________ Contract: ____________
Lab Code: ________ Case No.: ________ SAS No.: ________ SDG No.: ________
Matrix Spike - EPA Sample No.: ________

COMPOUND	SPIKE ADDED (ug/L)	SAMPLE CONC. (ug/L)	MS CONC. (ug/L)	MS% REC#	QC LIMITS REC.
Phenol					12-89
2-Chlorophenol					27-123
1,4-Dichlorobenzene					36-97
N-Nitroso-di-n-propylamine					41-116
1,2,4-Trichlorobenzene					39-98
4-Chloro-3-methylphenol					23-97
Acenaphthene					46-118
4-Nitrophenol					10-80
2,4-Dinitrotoluene					24-96
Pentachlorophenol					9-103
Pyrene					26-127

COMPOUND	SPIKE ADDED (ug/L)	MSD CONC. (ug/L)	MSD% REC	% RPD#	QC LIMITS	
					RPD	REC.
Phenol					42	12-89
2-Chlorophenol					40	27-123
1,4-Dichlorobenzene					28	36-97
N-Nitroso-di-n-propylamine					38	41-116
1,2,4-Trichlorobenzene					28	39-98
4-Chloro-3-methylphenol					42	23-97
Acenaphthene					31	46-118
4-Nitrophenol					50	10-80
2,4-Dinitrotoluene					38	24-96
Pentachlorophenol					50	9-103
Pyrene					31	26-127

#Column to be used to flag recovery and RPD values with an asterisk
*Values outside of QC limits

RPD: ________ out of ________ outside limits
Spike Recovery: ________ out of ________ outside limits

COMMENTS: ____________

FORM III SV-1 1/87 Rev.

Figure 14. Water Semivolatile MS/MSD Recovery

SOIL SEMIVOLATILE MATRIX SPIKE/MATRIX SPIKE DUPLICATE RECOVERY

Lab Name: ____________________ Contract: ____________
Lab Code: ________ Case No.: ______ SAS No.: ______ SDG No.: ______
Matrix Spike - EPA Sample No.: ________ Level: (low/med) __________

COMPOUND	SPIKE ADDED (ug/kg)	SAMPLE CONC. (ug/kg)	MS CONC. (ug/kg)	MS% REC#	QC LIMITS REC.
Phenol					26-90
2-Chlorophenol					25-102
1,4-Dichlorobenzene					28-104
N-Nitroso-di-n-propylamine					41-126
1,2,4-Trichlorobenzene					38-107
4-Chloro-3-methylphenol					26-103
Acenaphthene					31-137
4-Nitrophenol					11-114
2,4-Dinitrotoluene					28-89
Pentachlorophenol					17-109
Pyrene					35-142

COMPOUND	SPIKE ADDED (ug/kg)	MSD CONC. (ug/kg)	MSD% REC#	% RPD#	QC LIMITS	
					RPD	REC.
Phenol					35	26-90
2-Chlorophenol					50	25-102
1,4-Dichlorobenzene					27	28-104
N-Nitroso-di-n-propylamine					38	41-126
1,2,4-Trichlorobenzene					23	38-107
4-Chloro-3-methylphenol					33	26-103
Acenaphthene					19	31-137
4-Nitrophenol					50	11-114
2,4-Dinitrotoluene					47	28-89
Pentachlorophenol					47	17-109
Pyrene					36	35-142

#Column to be used to flag recovery and RPD values with an asterisk
*Values outside of QC limits

RPD: ______ out of ______ outside limits
Spike Recovery: ______ out of ______ outside limits

COMMENTS: ____

FORM III SV-2 1/87 Rev.

Figure 15. Soil Semivolatile MS/MSD Recovery

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PESTICIDES/PCBs

The analytical methods that follow are designed to analyze water, soil and sediment for the organic compounds listed in Table D-3. The methods include the following: "Sample Preparation for Pesticides/PCBs in Water," "Sample Preparation for Pesticides/PCBs in Soil/Sediment," "Screening of Pesticide/PCB Extracts," and "GC/EC Analysis of Pesticides/PCBs." The methods are derived from the U.S. EPA's CLP Statement of Work for Organics Analysis (October 1986).

Problems have been associated with the following compounds covered by these methods. Alpha-BHC, gamma-BHC, Endosulfan I and II, and Endrin are subject to decomposition under alkaline conditions.

Because weathering and/or different formulations of chlordane usually modify the chromatographic pattern exhibited by technical chlordane, the use of these methods is not appropriate for the determination of technical chlordane. The analysis of the isomers alpha-chlordane and gamma-chlordane by this method is appropriate, however.

Table D-3. Analytes Determined by CLP Pesticides/PCBs Analysis Method

		Contract Required Detection Limits[a]	
Analyte	CAS Number	Water (ug/L)	Low Soil/Sediment[b,c] (ug/kg)
100. alpha-BHC	319-84-6	0.05	8.0
101. beta-BHC	319-85-7	0.05	8.0
102. delta-BHC	319-86-8	0.05	8.0
103. gamma-BHC (Lindane)	58-89-9	0.05	8.0
104. Heptachlor	76-44-8	0.05	8.0
105. Aldrin	309-00-2	0.05	8.0
106. Heptachlor epoxide	1024-57-3	0.05	8.0
107. Endosulfan I	959-98-8	0.05	8.0
108. Dieldrin	60-57-1	0.10	16.0
109. 4,4'-DDE	72-55-9	0.10	16.0
110. Endrin	72-20-8	0.10	16.0
111. Endosulfan II	33213-65-9	0.10	16.0
112. 4,4'-DDD	72-54-8	0.10	16.0
113. Endosulfan sulfate	1031-07-8	0.10	16.0
114. 4,4'-DDT	50-29-3	0.10	16.0
115. Endrin ketone	53494-70-5	0.10	16.0
116. Methoxychlor	72-43-5	0.5	80.0
117. alpha-chlordane	5103-71-9	0.5	80.0
118. gamma-chlordane	5103-74-2	0.5	80.0
119. Toxaphene	8001-35-2	1.0	160.0
120. Aroclor-1016	12674-11-2	0.5	80.0
121. Aroclor-1221	11104-28-2	0.5	80.0
122. Aroclor-1232	11141-16-5	0.5	80.0
123. Aroclor-1242	53469-21-9	0.5	80.0
124. Aroclor-1248	12672-29-6	0.5	80.0
125. Aroclor-1254	11097-69-1	1.0	160.0
126. Aroclor-1260	11096-82-5	1.0	160.0

a. Specific detection limits are highly matrix dependent. The detection limits listed herein are provided for guidance and may not always be achievable.

b. Detection limits listed for soil/sediment are based on wet weight. The detection limits calculated by the laboratory for soil/sediment, calculated on dry weight basis as required by the contract, will be higher.

c. Contract detection limits (CRDL) for pesticides/PCBs at medium levels in soil/sediment are 15 times the listed CRDL for pesticides/PCBs at low levels in soil/sediment.

SAMPLE PREPARATION FOR PESTICIDES/PCBs IN WATER

1.0 SUMMARY OF METHOD

1.1 A measured volume of sample, approximately 1 L, is solvent extracted with methylene chloride using a separatory funnel or a continuous extractor. The methylene chloride extract is dried, exchanged to hexane, and adjusted to a final volume of 10 mL. The extract for pesticide/PCB analysis may be prepared from an aliquot of the extract for semivolatiles, or in a separate extraction procedure. If it is prepared from the semivolatile extract, refer to the methods for extraction of semivolatiles.

2.0 INTERFERENCES

2.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks. Interferences by phthalate esters can pose a major problem in pesticide analysis when using the electron capture detector. These compounds generally appear in the chromatogram as broad eluting peaks. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled. Interferences from phthalates can best be minimized by avoiding the use of plastics in the laboratory. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination.

2.2 Matrix interference may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the site being sampled. The cleanup procedure in

Section 6.3 must be used to overcome such interferences to attem[illegible] to achieve the contract required determination limits (CRDLs). The cleanup procedure in Section 6.4 may be used to remove sulfur interferences.

3.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

3.1 Sample Storage

The samples must be protected from light and refrigerated at 4°C (±2°C) from the time of receipt until extraction and analysis.

3.2 Holding Times

3.2.1 If separatory funnel procedures are employed for extractions for pesticide/PCB analyses, extraction of water samples shall be completed within 5 days of the validated time of sample receipt (VTSR). If continuous liquid-liquid extraction procedures are employed, extraction of water samples shall be started within 5 days of VTSR.

3.2.2 Extracts of water samples must be analyzed within 40 days of VTSR.

4.0 APPARATUS AND EQUIPMENT

4.1 Glassware (Brand names and catalog numbers included for illustration purposes only)

4.1.1 Separatory funnel - 2000 mL with Teflon stopcock.

4.1.2 Drying column - Chromatographic column approximately 400-mm long x 19-mm I.D., with coarse frit. (Substitution of a small pad of disposable Pyrex glass wool for the frit will help prevent cross-contamination of sample extracts.)

4.1.3 Concentrator tube - Kuderna-Danish, 10 mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground-glass stopper is used to prevent evaporation of extracts.

4.1.4 Evaporative flask - Kuderna-Danish, 500 mL (Kontes K-5700010500 or equivalent). Attach to concentrator tube with springs.

4.1.5 Snyder column - Kuderna-Danish, three-ball macro (Kontes K-503000-0121 or equivalent).

4.1.6 Snyder column - Kuderna-Danish, two-ball micro (Kontes K-569001-0219 or equivalent).

4.1.7 Continuous liquid-liquid extractors - Equipped with Teflon or glass connecting joints and stopcocks requiring no lubrication. (Hershberg-Wolf Extractor-Ace Glass Company, Vineland, NJ P/N 6841-10, or equivalent.)

4.1.8 Vials - Amber glass, 10- to 15-mL capacity, with Teflon-line screw cap.

4.1.9 Bottle or test tube - 50 mL with Teflon-lined screw cap for sulfur removal.

4.1.10 Chromatographic column for alumina - 8-mL (200-mm x 8-mm I.D.) Polypropylene column (Kontes K-420160 or equivalent) or 6-mL (150-mm x 8-mm I.D.) glass column (Kontes K-420155 or equivalent), or 5-mL serological pipets plugged with a small piece of Pyrex glass wool in the tip. The Kontes columns may be plugged with Pyrex glass wool or a polyethylene porous disk (Kontes K-420162).

4.2 Pyrex glass wool - Pre-rinse glass wool with appropriate solvents to ensure its cleanliness.

4.3 Silicon carbide boiling chips - Approximately 10/40 mesh. Heat to 400°C for 30 min or Soxhlet extract with methylene chloride.

4.4 Water bath - Heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.

4.5 Balance - Analytical, capable of accurately weighing 0.0001 g.

4.6 Nitrogen evaporation device - Equipped with a water bath that can be maintained at 35 to 40°C. The N-Evap or Organomation Associates, Inc. South Berlin, MA (or equivalent) is suitable.

5.0 REAGENTS

5.1 Reagent water - Reagent water is defined as a water in which an interferent is not observed at or above the CRDL of each parameter of interest.

5.2 Acetone, hexane, isooctane (2,2,4-trimethylpentane), methylene chloride - Pesticide quality or equivalent.

5.3 Sodium sulfate - (ACS) Granular, anhydrous. Purify by heating at 400°C for 4 h in a shallow tray.

5.4 Alumina - Neutral, Super I Woelm or equivalent. (Universal Scientific, Incorporated, Atlanta, Georgia or equivalent.) Prepare activity III by adding 7 percent (v/w) reagent water to the Super I neutral alumina. Tumble or shake in a wrist action shaker for a minimum of 2 h or preferably overnight. There should be no lumps present. Store in a tightly sealed glass container. A 25-cycle Soxhlet extraction of the alumina with methylene chloride is required if a solvent blank analyzed by the pesticide technique indicates any interferences for the compounds of interest.

5.4.1 Alumina equivalency check - Test the alumina by adding the following surrogate standards in 1:1 acetone/hexane to the alumina and following Section 6.3.

phenol-d_5	nitrobenzene-d_5
2,4,6-tribromophenol	terphenyl-d_{14}
2-fluorophenol	2-fluorobiphenyl

The tribromophenol should not be detected by GC/EC if the alumina and its activation are acceptable. Also check recovery of all single component pesticides following the same procedure. The percent recovery for all single component pesticides must be $\geq$80 percent, except for endosulfan sulfate which must be $\geq$60 percent and endrin aldehyde which is not recovered. The data must be retained by the laboratory and made available for inspection during on-site evaluations.

5.5 Sodium hydroxide solution (10 N) - (ACS) Dissolve 3.30 g of tetrabutylammonium hydrogen sulfate in 100 mL of distilled water.

5.6 Tetrabutylammonium (TBA) - Sulfite reagent. Dissolve 3.39 g of tetrabutylammonium hydrogen sulfate in 100 mL of distilled water. To remove impurities, extract this solution three times with 20-mL portions of hexane. Discard the hexane extracts, and add 25 g of sodium sulfite to the water solution. Store the resulting solution, which is saturated with sodium sulfite, in an amber bottle with a Teflon-lined screw cap. This solution can be stored at room temperature for at least 1 month.

5.7 Pesticide surrogate standard spiking solution

5.7.1 The surrogate standard is added to all samples and calibration solutions; the compound specified for this purpose is dibutylchlorendate.

5.7.2 Prepare a surrogate standard spiking solution at a concentration of 1 ug/mL in acetone. Store the spiking solutions at 4°C (±2°C) in Teflon-sealed containers. The solutions should be checked frequently for stability. These solutions must be replaced after 12 months, or sooner if comparison with quality control check samples indicates a problem.

5.8 Sulfuric acid solution (1 + 1) - Slowly, add 50 mL of H_2SO_4 (sp gr 1.84) to 50 mL of reagent water.

5.9 Pesticide matrix standard spiking solution. Prepare a spiking solution of acetone or methanol that contains the following pesticides in the concentrations specified.

Pesticide	Concentration (ug/mL)
Lindane	0.2
Heptachlor	0.2
Aldrin	0.2
Dieldrin	0.5
Endrin	0.5
4,4'-DDT	0.5

Matrix spikes are also to serve as duplicates by spiking two 1-L portions from the one sample chosen for spiking.

6.0 PROCEDURE

6.1 Separatory Funnel Extraction

6.1.1 Samples may be extracted using separatory funnel techniques. If emulsions prevent acceptable solvent recovery with separatory funnel extractions, continuous liquid-liquid extraction (Section 6.2) may be used. The separatory funnel extraction scheme described below assumes a sample volume of one liter. Note: If the pesticide/PCB extract is prepared from an aliquot of the semivolatile extract, refer to the semivolatile methods, as well as these procedures.

6.1.2 Using a 1-L graduated cylinder, measure out a 1-L sample aliquot and place it into a 2-L separatory funnel. Pipet 1.0 mL of surrogate standard spiking solution into the separatory funnel and mix well. Check the pH of the sample with wide range pH paper and adjust to between 5 and 9 pH with 10 N sodium hydroxide and/or sulfuric acid solution (1 + 1). (Note: Recovery of dibutylchlorendate will be low if pH is outside this range.) Add 1.0 mL of pesticide matrix spiking solution to each of two 1-L portions from the sample selected for spiking.

6.1.3 Add 60 mL of methylene chloride to the separatory funnel and extract the sample by shaking the funnel for 2 min, with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical means. Drain methylene chloride into a 250-mL Erlenmeyer flask.

6.1.4 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

6.1.5 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D if equivalency is demonstrated for all pesticides listed in Table D-3.

6.1.6 Pour the combined extract through a drying column containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

6.1.7 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (80 to 90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 to 15 min. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus. Allow it to drain and cool for at least 10 min.

6.1.8 Momentarily remove the Snyder column, add 50 mL of hexane and a new boiling chip and re-attach the Snyder column. Pre-wet the column by adding about 1 mL of hexane to the top. Concentrate the solvent extract as before. The elapsed time of concentration should be 5 to 10 min. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool at least 10 min.

6.1.9 Remove the Snyder column, rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of hexane. If sulfur crystals are a problem, proceed to Section 6.4.1; otherwise continue to Section 6.1.10.

6.1.10 Nitrogen blowdown concentration - Place the concentrator tube in a warm water bath (35°C) and evaporate the solvent volume to 0.5 mL using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon). Caution: New plastic tubing must not be used between the carbon trap and the sample, as it may introduce interferences. The internal wall of the tube must be rinsed down several times with hexane during the operation and the final volume brought to 0.5 mL. During evaporation, the tube solvent level must be kept below the water level of the bath. The extract must never be allowed to become dry.

6.1.11 Dilute the extract to 1 mL with acetone and proceed to Section 6.3.

6.2 Continuous Liquid-Liquid Extraction

6.2.1 When experience with a sample from a given source indicates that a serious emulsion problem will result, or if an emulsion is encountered in Section 6.1.3 using a separatory funnel, a continuous extractor should be used.

6.2.2 Using a 1-L graduated cylinder, measure out a 1-L sample of aliquot and place it into the continuous extractor. Pipet 1.0 mL of surrogate standard spiking solution into the continuous extractor and mix well. Check the pH of the sample with wide range pH paper and adjust to between 5 and 9 pH with 10 N sodium hydroxide and/or sulfuric acid solution (1 + 1).

6.2.3 Add 500 mL of methylene chloride to the distilling flask. Add sufficient reagent water to ensure proper operation and extract for 18 h. Allow to cool, then detach the boiling flask and dry. Concentrate the extract as in Sections 6.1.5 to 6.1.11.

6.3 Alumina Column Cleanup

6.3.1 Add 3 g of activity III neutral alumina to the 10-mL chromatographic column. Tap the column to settle the alumina. Do not pre-wet the alumina.

6.3.2 Transfer the 1 mL of hexane/acetone extract from Section 6.1.11 to the top of the alumina using a disposable Pasteur pipet. Collect the eluate in a clean 10-mL concentrator tube.

6.3.3 Add 1 mL of hexane to the original extract concentrator tube to rinse it. Transfer these rinsings to the alumina column. Elute the column with an additional 9 mL of hexane. Do not allow the column to go dry during the addition and elution of the sample.

6.3.4 Adjust the extract to a final volume of 10 mL using hexane.

6.3.5 The pesticide/PCB fraction is ready for analysis. Proceed to the method "GC/EC Analysis of Pesticides/PCBs."

Store the extracts at 4°C (± 2°C) in the dark in Teflon-sealed containers until analyses are performed.

6.4 Optional Sulfur Cleanup

6.4.1 Concentrate the hexane extract from Section 6.1.9 to 1 mL.

6.4.2 Transfer the 1 mL to a 50-mL clear glass bottle or vial with a Teflon-lined screw cap. Rinse the concentrator tube with 1 mL of hexane, adding the rinsings to the 50-mL bottle.

6.4.3 Add 1 mL of TBA-sulfite reagent and 2 mL of 2-propanol, cap the bottle, and shake for at least 1 min. If the sample is colorless or if the initial color is unchanged, and if clear crystals (precipitated sodium sulfite) are observed, sufficient sodium sulfite is present. If the precipitated sodium sulfite disappears, add more crystalline sodium sulfite in approximately 100-mg portions until a solid residue remains after repeated shaking.

6.4.4 Add 5 mL of distilled water and shake for at least 1 min. Allow the sample to stand 5 to 10 min. Transfer the hexane layer (top) to a concentrator ampul and go back to Section 6.1.10.

MEDIUM LEVEL PREPARATION FOR ANALYSIS OF PESTICIDES/PCBs IN SOIL/SEDIMENT

1.0 SCOPE AND APPLICATION

1.1 This procedure is designed for the preparation of sediment/soil samples which may contain pesticides/PCBs at a level greater than 1,000 ug/kg.

1.2 Samples to be prepared and analyzed by this method must be screened to determine whether sufficient quantities of pesticides/PCBs are present to warrant analysis by the medium level protocol. The use of gas chromatography with electron capture detection (GC/EC) is recommended for screening soil/sediment samples for pesticides/PCBs; however, the analyst is at liberty to determine the specific method of characterization. If the screenings indicate no detectable pollutants at a level of quantitation of <1000 ug/kg, the sample should be prepared by the low level method.

1.3 If the extract for pesticide/PCB analysis is to be prepared from an aliquot of the semivolatile extract, also refer to the specific instructions in the semivolatile methods.

2.0 SUMMARY OF METHOD

2.1 Portions of soil/sediment are extracted and screened by methods of the contractor's choice.

2.2 If pesticides/PCBs are detected in the screen at levels above approximately 1000 ug/kg, a 1-g sample is extracted with 10.0 mL of hexane for analysis by GC/EC.

2.3 If no pesticides/PCBs are detected above 1000 ug/kg, then the sample shall be prepared by the low level protocol.

3.0 INTERFERENCES

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the total ion current profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks. Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source.

3.2 The procedure is designed to allow quantitation limits as low as 1000 ug/kg for pesticides/PCBs. If peaks are present based on GC screen, the sample is determined to require a medium level analysis by GC/EC. Some samples may contain high concentrations of chemicals that interfere with the analysis of other components at lower levels; the quantitation limits in those cases may be significantly higher.

4.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

4.1 Sample Storage - The samples must be protected from light and refrigerated at 4°C (+2°C) from the time of receipt until extraction and analysis.

4.2 Holding Times

4.2.1 If separatory funnel procedures are employed for extractions for pesticide/PCB analyses, extraction of soil/sediment samples shall be completed within 10 days of validated time of sample receipt (VTSR). If continuous liquid-liquid extraction procedures are employed, extraction of soil/sediment samples shall be started within 10 days of VTSR.

4.2.2 Extracts of soil/sediment samples must be analyzed within 40 days of VTSR.

5.0 APPARATUS AND EQUIPMENT

5.1 Glass scintillation vials - At least 20 mL, with screw cap and Teflon or aluminum foil liner.

5.2 Spatula - Stainless steel or Teflon.

5.3 Balance - Capable of weighing 100 g to the nearest 0.01 g.

5.4 Vials and caps - 2 mL for GC autosampler.

5.5 Pasteur pipet - Disposable glass wool rinsed with methylene chloride.

5.6 Concentrator tubes - 15 mL.

5.7 Ultrasonic cell disruptor - Heat Systems Ultrasonics, Inc., Model W-375 SONICATOR or equivalent (375 Watt with pulsing capability, No. 200 1/2-in. tapped disruptor horn, and No. 419 1/8-in. standard tapered MICROTIP probe). Note: To ensure that sufficient energy is transferred to the sample during extraction, the MICROTIP probe must be replaced if the tip begins to erode. Erosion of the tip is evidenced by a rough surface.

5.8 Sonabox - Recommended with above disruptors for decreasing cavitation sound.

5.9 Test tube rack.

5.10 Oven - Drying.

5.11 Desiccator.

5.12 Crucibles - Porcelain.

5.13 Chromatography column for alumina - 8-mL (200-mm x 8-mm I.D.) Polypropylene column (Kontes K-420160 or equivalent) or 6-mL (150-mm x 8-mm I.D.) glass column (Kontes K-420155 or equivalent) or 5-mL serological pipets plugged with a small piece of Pyrex glass wool in the tip. (Pyrex glass wool shall be pre-rinsed with appropriate solvents to ensure its cleanliness). The Kontes columns may be plugged with Pyrex glass wool or a polyethylene porous disk (Kontes K420162).

6.0 REAGENTS

6.1 Sodium sulfate - Anhydrous powdered reagent grade, heated at 400°C for 4 h, cooled in a desiccator, and stored in a glass bottle (Baker anhydrous powder, catalog 3898 or equivalent).

6.2 Methylene chloride, hexane, methanol, and acetone - Pesticide residue analysis grade or equivalent.

6.3 Pesticide/PCB Surrogate Standard Spiking Solution

6.3.1 The compound specified is dibutylchlorendate. Prepare a solution at a concentration of 20 ug/mL in methanol. Store the spiking solutions at 4°C (±2°C) in Teflon-sealed containers. The solutions should be checked frequently for stability. These solutions must be replaced after 12 months, or sooner, if comparison with quality control check samples indicates a problem.

6.4 Pesticide/PCB Matrix Standard Spiking Solution

6.4.1 Prepare a spiking solution in methanol that contains the following pesticides in the concentrations specified below. Store the spiking solutions at 4°C (±2°C) in Teflon-sealed containers.

6.4.2 These solutions should be checked frequently for stability. These solutions must be replaced after 12 months, or sooner, if comparison with quality control check samples indicates a problem.

Pesticide	Concentration (ug/mL)
Lindane	2.0
Heptachlor	2.0
Aldrin	2.0
Dieldrin	5.0
Endrin	5.0
4,4'-DDT	5.0

6.5 Alumina - Neutral, super I Woelm (Universal Scientific, Atlanta, GA) or equivalent. Prepare activity III by adding 7 percent (v/w) reagent water to the Super I neutral alumina. Tumble or shake on a wrist action shaker for a minimum of 2 h or preferably overnight. There should be no lumps present. Store in a tightly sealed glass container. A 25-cycle Soxhlet extraction of the alumina with methylene chloride is required if a solvent blank analyzed by the pesticide techniques indicates any interferences for the compounds of interest.

6.5.1 Alumina Equivalency Check. Test the alumina by adding the following surrogate standards in 1:1 acetone/hexane to the alumina and following Section 7.8.

phenol-d_5
2,4,6-tribromophenol
2-fluorophenol
nitrobenzene-d_5
terphenyl-d_{14}
2-fluorobiphenyl

The tribromophenol should not be detected by GC/EC if the alumina and its activation are acceptable. Also check recovery of all single component pesticides following the same procedure. The percent recovery for all single

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component pesticides must be >80 percent, except for endosulfan sulfate which must be >60 percent and endrin aldehyde which is not recovered. The data must be retained by the laboratory and made available for inspection during on-site evaluations.

6.6 Reagent Water - Reagent water is defined as water in which an interferent is not observed at or above the contract required detection limits (CRDL) of each parameter of interest.

7.0 PROCEDURE

7.1 Transfer the sample container into a fume hood. Open the sample vial and mix the sample. Transfer approximately 1 g (record weight to nearest 0.1 g) of sample to a 20-mL vial. Wipe the mouth of the vial with a tissue to remove any sample material. Record the exact weight of the sample taken. Cap the vial before proceeding with the next sample to avoid any cross contamination.

7.1.1 Transfer 50 g of soil/sediment to 100-mL beaker. Add 50 mL of water and stir for 1 h. Determine pH of sample with glass electrode and pH meter while stirring. Report pH value on appropriate data sheets. If the pH of the soil is greater than 11 or less than 5, contact the Project Manager for instructions on how to handle the sample. Document the instructions. Discard this portion of sample. Note: Recovery of dibutylchlorendate will be low if pH is outside this range.

7.2 Add 2 g of anhydrous powdered sodium sulfate to the sample and mix well.

7.3 Surrogate standards are added to all samples, spikes, and blanks. Add 50 uL of surrogate spiking solution to the sample mixture.

7.4 Add 1.0 mL of matrix standard spiking solution to each of two 1-g portions from the sample chosen for spiking.

7.5 Immediately add 10.0 mL (only 9.0 mL for the matrix spiked sample) of hexane to the sample and disrupt the sample with the 1/8-inch tapered MICROTIP ultrasonic probe for 2 min with output control setting at "5," mode switch on "pulse," and percent duty cycle set at 50 percent. (If using a sonicator other than Model W-375, refer to the manufacturer's instructions for appropriate output settings.) Before extraction, make certain that the sodium sulfate is free flowing and not a consolidated mass. As required, break up large lumps with a clear spatula, or very carefully with the tip of the probe.

7.6 Loosely pack disposable Pasteur pipets with 2- to 3-cm glass wool plugs. Filter the extract through the glass wool and collect at approximately 5 mL in a concentrator tube.

7.7 Transfer 1.0 mL of the hexane extract to a glass concentrator tube and concentrate to 0.5 mL using nitrogen blowdown concentration. Add 0.5 mL of acetone to 0.5 mL of hexane extract. Swirl to mix. The pesticide extract must now be passed through an alumina column to remove polar interferences.

7.8 Alumina Column Cleanup

7.8.1 Add 3 g of activity III neutral alumina to the 10-mL chromatographic column. Tap the column to settle the alumina. Do not pre-wet the alumina.

7.8.2 Transfer the 1.0 mL of hexane/acetone extract from Section 7.7 to the top of the alumina using a disposable Pasteur pipet. Collect the eluate in a clean, 10-mL concentrator tube.

7.8.3 Add 1 mL of hexane to the original extract concentrator tube to rinse it. Transfer these rinsings to the alumina column. Elute the column with an additional 9 mL of hexane. Do not allow the column to go dry during the addition and elution of the sample.

7.8.4 Concentrate the extract to 1.0 mL using hexane where methylene chloride is specified. When concentrating medium level extract, the nitrogen blowdown technique should be used to avoid contaminating the micro-Snyder column.

7.9 Observe the Appearance of the Extract

7.9.1 If crystals of sulfur are evident or sulfur is expected to be present, proceed to Section 7.10.

7.9.2 If the sulfur is not expected to be a problem, transfer the 1.0 mL to a GC vial and label as pesticide/PCB fraction. The extract is ready for GC/EC analysis. Store the extracts at $4^{\circ}C$ ($\pm 2^{\circ}C$) in the dark until analyses are performed.

7.10 Optional Sulfur Cleanup

7.10.1 Transfer the 1.0-mL extract from Section 7.9.1 to a 50-mL clear glass bottle or vial with a Teflon-lined screw cap. Rinse the concentrator tube with 1.0 mL of hexane, adding the rinsings to the 50-mL bottle. If only a partial set of samples requires sulfur cleanup, set up a new reagent blank with 1.0 mL of hexane and take it through the sulfur cleanup. Include the surrogate standards.

7.10.2 Add 1 mL of TBA-sulfite reagent and 1 mL of 2-propanol, cap the bottle, and shake for at least 1 min. If the sample is colorless or if the initial color is unchanged and if clear crystals (precipitated sodium sulfite) are observed, sufficient sodium sulfite is present. If the precipitated sodium sulfite disappears, add more crystalline sodium sulfite in approximately 100-mg portions until a solid residue remains after repeated shaking.

7.10.3 Add 5 mL of distilled water and shake for at least 1 min. Allow the sample to stand for 5 to 10 min and remove the hexane layer (top) for analysis. Concentrate the hexane to 1.0 mL in Kuderna-Danish apparatus or by nitrogen blowdown technique using hexane where methylene chloride is specified. The temperature for the water bath should be about 80°C for the micro-Snyder column technique. Continue as outlined in Section 7.9.2.

LOW LEVEL PREPARATION FOR ANALYSIS OF PESTICIDES/PCBs IN SOIL/SEDIMENT

1.0 SUMMARY OF METHOD

1.1 If based on the results of a screen by gas chromatography with electron capture detection (GC/EC), no pesticides/PCBs are present in the sample above 1000 ug/kg, a 30-g portion of soil/sediment is mixed with anhydrous powdered sodium sulfate and extracted with 1:1 methylene chloride/acetone using an ultrasonic probe. The extract is concentrated and an optional gel-permeation column cleanup may be used. The extract is cleaned up using a micro alumina column and analyzed by GC/EC for pesticides.

2.0 INTERFERENCES

2.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the total ion current profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks. Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source.

3.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

3.1 The samples must be protected from light and refrigerated at 4°C (±2°C) from the time of receipt until extraction and analysis.

3.2 Holding Times

3.2.1 If separatory funnel procedures are employed for extractions for pesticide/PCB analyses, extraction of soil/sediment samples shall be completed within 10 days of VTSR. If continuous liquid-liquid extraction procedures are employed, extraction of soil/sediment samples shall be started within 10 days of VTSR.

3.2.2 Extracts of soil/sediment samples must be analyzed within 40 days of VTSR.

4.0 APPARATUS AND EQUIPMENT

4.1 Apparatus for Determining Percent Moisture

4.1.1 Oven - Drying.

4.1.2 Desiccator.

4.1.3 Crucibles - Porcelain.

4.2 Pasteur pipet - 1 mL, disposable glass.

4.3 Ultrasonic cell disruptor - Heat Systems Ultrasonics, Inc., Model W-375 SONICATOR or equivalent (375 watt with pulsing capability, No. 305 1/4-in. tapped high gain "Q" disruptor horn or Model 208 3/4-in. standard tip solid horn). Note: To ensure that sufficient energy is transferred to the sample during extraction, the probe must be replaced if the tip begins to erode. Erosion of the tip is evidenced by a rough surface.

4.4 Beakers - 400 mL.

4.5 Vacuum Filtration Apparatus

4.5.1 Buchner funnel.

4.5.2 Filter paper - Whatman No. 41 or equivalent.

4.6 Kuderna-Danish (K-D) Apparatus

4.6.1 Concentrator tube - 10 mL, graduated (Kontes K-570001-0500-1025 or equivalent).

4.6.2 Evaporative flask - 500 mL (Kontes K-570001-0500 or equivalent).

4.6.3 Snyder column - Three-ball macro (Kontes K-503000-0121 or equivalent).

4.6.4 Snyder column - Two-ball micro (Kontes K-569001-0219 or equivalent).

4.7 Silicon carbide boiling chips - Approximately 10/40 mesh. Heat to 400°C for 30 min or Soxhlet extract with methylene chloride.

4.8 Water bath - Heated, with concentric ring cover capable of temperature control (±2°C). The bath should be used in a hood.

4.9 Balance - Capable of accurately weighing ±0.01 g.

4.10 Vials and caps - 2 mL for GC autosampler.

4.11 Balance - Analytical, capable of accurately weighing ±0.0001 g.

4.12 Nitrogen evaporation device equipped with a water bath that can be maintained at 35 to 40°C. The N-Evap by Organomation Associates, Inc. South Berlin, MA (or equivalent) is suitable.

4.13 Gel permeation chromatography (GPC) cleanup device. Note: GPC cleanup is highly recommended for all extracts of low level soils.

4.13.1 Automated System

4.13.1.1 Gel-permeation chromatograph - Analytical Biochemical Labs, Inc., GPC Autoprep 1002 or equivalent including:

4.13.1.1.1 Column - 25-mm x 600- to 700-mm glass packed with 70 g of Bio-Beads SX-3.

4.13.1.1.2 Syringe - 10 mL with Luerlook fitting.

4.13.1.1.3 Syringe filter holder and filters - Stainless steel and TFE, Gelman 4310 or equivalent.

4.13.2 Manual System Assembled from Parts*

4.13.2.1 Column - 25-mm I.D. x 600- to 700-mm heavy wall glass packed with 70 g of Bio-Beads SX-3.

4.13.2.2 Pump - Altex Scientific, Model No. 1001A, semi-preparative, solvent metering system. Pump capacity, 28 mL/min.

4.13.2.3 Detector - Altex Scientific, Model No. 153 with 254 nm UV source and 8-uL semi-preparative flow-cells (2-mm pathlengths).

4.13.2.4 Microprocessor/controller - Altex Scientific, Model No. 420, Microprocessor System Controller, with extended memory.

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*Wise, R. H., D. F. Bishop, R. T. Williams and B. M. Austern, "Gel Permeation Chromatography in the GC/MS Analysis of Organics in Sludges" U.S. EPA, Municipal Environmental Research Laboratory - Cincinnati, Ohio 45268.

4.13.2.5 Injector - Altex Scientific, Catalog No. 201-56, sample injection valve, Tefzel, with 10-mL sample loop.

4.13.2.6 Recorder - Linear Instruments, Model No. 385, 10-in. recorder.

4.13.2.7 Effluent Switching Valves - Teflon slider valve, 3-way with 0.060-in. ports.

4.13.2.8 Supplemental Pressure Gauge with connecting Tee - U.S. Gauge, 0.200 psi, stainless steel. Installed as a downstream monitoring device between column and detector. Flow rate was typically 5 mL/min of methylene chloride. Recorder chart speed was 0.50 cm/min.

4.13.3 Chromatography column for alumina - 8-mL (200-mm x 8-mm I.D.) polypropylene column (Kontes K-420160 or equivalent) or 6-mL (150-mm x 8-mm I.D.) glass column (Kontes K-420155 or equivalant) or 5-mL serological pipets plugged with a small piece of Pyrex glass wool in the tip. (Pyrex glass wool shall be pre-rinsed with appropriate solvents to ensure its cleanliness). The Kontes columns may be plugged with Pyrex glass wool or a polyethylene porous disk (Kontes K-420162).

4.13.4 Pyrex glass wool.

4.13.5 Bottle or test tube - 50 mL with Teflon-lined screw cap for sulfur removal.

4.13.6 Pasteur pipets - Disposable.

5.0 REAGENTS

5.1 Sodium sulfate - Anhydrous powdered reagent grade, heated at 400°C for 4 h, cooled in a desiccator, and stored in a glass bottle (Baker anhydrous powder, Catalog No. 73898 or equivalent).

5.2 Methylene chloride, hexane, acetone, isooctane, 2-propanol and benzene - Pesticide quality or equivalent.

5.3 Alumina - Neutral, super I Woelm (Universal Scientific, Atlanta, GA) or equivalent. Prepare activity III by adding 7 percent (v/w) reagent water to the Super I neutral alumina. Tumble or shake on a wrist action shaker for a minimum of 2 h or preferably overnight. There should be no lumps present. Store in a tightly sealed glass container. A 25-cycle Soxhlet extraction of the alumina with methylene chloride is required if a solvent blank analyzed by the pesticide techniques indicates any interferences for the compounds of interest.

5.3.1 Alumina Equivalency Check. Test the alumina by adding the surrogate standards listed below in 1:1 acetone/hexane to the alumina and following Section 6.4.

phenol-d_5	nitrobenzene-d_5
2,4,6-tribromophenol	terphenyl-d_{14}
2-fluorophenol	2-fluorobiphenyl

The tribromophenol should not be detected by GC/EC if the alumina and its activation are acceptable. Also check the recovery of all single component pesticides following the same procedure. The percent recovery for all single component pesticides must be $\geq$80 percent except for endosulfan sulfate which must be $\geq$60 percent and endrin aldehyde which is not recovered. The data must be retained by the contractor and made available for inspection during on-site evaluations.

5.4 Reagent water - Reagent water is defined as water in which an interferent is not observed at or above the contract required determination limit (CRDL) of each parameter of interest.

5.5 Tetrabutylammonium (TBA) - Sulfite reagent. Dissolve 3.39 g of tetrabutylammonium hydrogen sulfate in 100 mL of distilled water. To remove impurities, extract this solution three times with 20-mL portions of hexane. Discard the hexane extracts, and add 25 g of sodium sulfite to the water solution. Store the resulting solution, which is saturated with sodium sulfite, in an amber bottle with a Teflon-lined screw cap. This solution can be stored at room temperature for at least one month.

5.6 GPC Calibration Solutions

5.6.1 Corn oil - 200 mg/mL in methylene chloride.

5.6.2 Bis(2-ethylhexylphthalate) and pentachlorophenol - 4.0 mg/mL in methylene chloride.

5.7 Sodium sulfite - Reagent grade.

5.8 Surrogate Standard Spiking Solution

5.8.1 The surrogate standard is added to all samples, blanks, matrix spike, matrix spike duplicates, and calibrations solutions; the compound specified for this purpose is dibutylchlorendate.

5.8.2 Prepare a surrogate standard spiking solution at a concentration of 20 ug/mL in methanol. Store the spiking solutions at 4°C (±2°C) Teflon-sealed containers. The solutions should be checked frequently for stability. These solutions must be replaced after 12 months, or sooner if comparison with quality control check samples indicates a problem.

5.9 Pesticide matrix standard spiking solution - Prepare a spiking solution in methanol that contains the following pesticides in the concentrations specified below. Store spiking solutions at 4°C (±2°) in Teflon-sealed containers. The solutions should be checked frequently for stability. These solutions must be replaced after 12 months, or sooner if comparison with quality control check samples indicates a problem.

Pesticide	Concentration (ug/mL)
Lindane	2.0
Heptachlor	2.0
Aldrin	2.0
Dieldrin	5.0
Endrin	5.0
4,4'-DDT	5.0

Matrix spikes are also to serve as duplicates, therefore, add volume specified in Section 6.1 to each of two 30-g portions from sample chosen for spiking.

6.0 PROCEDURE

6.1 Sample Extraction

6.1.1 Decant and discard any water layer on a sediment sample. Mix samples thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

6.1.1.1 Transfer 50 g of soil/sediment to a 100-mL beaker. Add 50 mL of water and stir for 1 h. Determine pH of sample with glass electrode and pH meter while stirring. Report pH value on appropriate data sheets. If the pH of the soil is greater than 11 or less than 5, contact the Project Manager for instructions on how to handle the sample. Document the instructions. Discard this portion of sample. Note: Recovery of dibutylchlorendate will be low if pH is outside this range.

6.1.2 The following step should be performed rapidly to avoid loss of the more volatile extractables. Weigh approximately 30 g of sample to the nearest 0.1 g into a 400-mL beaker and add 60 g of anhydrous powdered sodium sulfate. Mix well. The sample should have a sandy texture at this point. Immediately, add 100 mL of 1:1 methylene chloride/acetone to the sample.

6.1.2.1 Immediately after weighing the sample for extraction, weigh 5 to 10 g of the sediment into a tared crucible. Determine the percent moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing. Concentrations of individual analytes will be reported relative to the dry weight of sediment.

$$\text{Percent moisture} = \frac{\text{Weight of sample (g)} - \text{Weight of dry sample (g)}}{\text{Weight of sample}} \times 100$$

6.1.2.2 Weigh out two 30-g (record weight to nearest 0.1 g) portions for use as matrix and matrix spike duplicates. Follow Section 6.1.2. When using GPC cleanup, add 800 uL of the pesticide matrix spike to each of the other two portions. When not using GPC cleanup, add 400 uL of the pesticide matrix spike to each of the two portions.

6.1.2.3 When using GPC, add 200 uL of pesticide surrogate to the sample. When not using GPC, add 100 uL of pesticide surrogate to the sample.

6.1.3 Place the bottom surface of the tip of the 3/4-in. disruptor horn about 1/2 in. below the surface of the solvent but above the sediment layer.

6.1.4 Sonicate for 3 min using 3/4-in. disruptor horn with output control knob set at 10 and mode switch on "pulse" and percent duty cycle knob set at 50 percent. When using a sonicator other than Model W-375, refer to the manufacturer's instructions for appropriate output settings. Do not use the microtip probe.

6.1.5 Decant and filter extracts through Whatman No. 41 filter paper using vacuum filtration or centrifuge and decant extraction solvent.

6.1.6 Repeat the extraction two more times with 2 additional 100-mL portions of 1:1 methylene chloride/acetone. Before each extraction, make certain that the sodium sulfate is free flowing and not a consolidated mass. As required, break up large lumps with a clean spatula, or very carefully with the tip of the probe. Decant off the extraction solvent after each sonication. On the final sonication, pour the entire sample into the Buchner funnel and rinse with 1:1 methylene chloride/acetone.

6.1.7 Transfer the extract to a Kuderna-Danish (K-D) concentrator consisting of a 10-mL concentrator tube and a 500-mL evaporative flask. Other concentration devices or techniques may be used if equivalency is demonstrated for all method parameters.

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6.1.8 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Pre-wet the Snyder column by adding about 1 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (80 to 90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10 to 15 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min, and make up to 10-mL volume with methylene chloride.

6.1.9 If GPC cleanup is not used proceed to Section 6.3.

6.2 Extract Cleanup

6.2.1 Packing the column - Place 70 g of Bio Beads SX-3 in a 400-mL beaker. Cover the beads with methylene chloride; allow the beads to swell overnight (before packing the columns). Transfer the swelled beads to the column and start pumping solvent through the column from bottom to top, at 5.0 mL/min. After approximately 1 h, adjust the pressure on the column to 7 to 10 psi and pump an additional 4 h to remove air from the column. Adjust the column pressure periodically as required to maintain 7 to 10 psi.

6.2.2 Calibration of the column - Load 5 mL of the corn oil solution into sample loop No. 1 and 5 mL of the phthalate-phenol solution into loop No. 2. Inject the corn oil and collect 10-mL fractions (i.e., change fraction at 2-min intervals) for 36 min. Inject the phthalate-phenol solution and collect 15-mL fractions for 60 min. Determine the corn oil elution pattern by evaporation of each fraction to dryness followed by a gravimetric determination of the residue. Analyze the phthalate-phenol fractions by GC/FID on the DB-5 capillary column, a UV spectrophotometer, or a GC/MS system. Plot the concentration of each component in each fraction versus total eluent volume (or time) from the injection points. Choose a "dump time" which allows ≥85 percent removal of the corn oil and ≤85 percent removal of the bis(2-ethylhexyl)-phthalate. Choose the "collect time" to extend at least 10 min after the elution of pentachlorophenol. Wash the column at least 15 min between samples. Typical parameters selected are dump time, 30 min (150 mL); collect time, 36 min (180 mL); and wash time, 15 min (75 mL). The column can also be calibrated by the use of a 254-mm UV detector in place of gravimetric and GC analyses of fractions. Measure the peak areas at various elution times to determine appropriate fractions.

The SX-3 Bio Beads column may be reused for several months, even if discoloration occurs. System calibration usually remains constant over this period of time if column flow rate remains constant.

6.2.3 Prefilter or load all extracts via the filter holder to avoid particulates that might stop the flow. Load one 5.0-mL aliquot of the extract onto the GPC column. Do not apply excessive pressure when loading the GPC. Purge the sample loading tubing thoroughly with solvent between extracts. After especially dirty extracts, run a GPC blank (methylene chloride) to check for carry-over. Process the extracts using the dump, collect, and wash parameters determined from the calibration and collect the cleaned extracts in 400-mL beakers tightly covered with aluminum foil. The phthalate-phenol calibration solution shall be taken through the cleanup cycle with each set of 23 extracts loaded into the GPC. The recovery for each compound must be >85 percent. This must be determined on a GC/FID, using a DB-5 capillary column, a UV recording spectrophotometer or a GC/MS system. A copy of the printouts of standard and check solution is required as a deliverable with each case. Show percent recovery on the copy.

6.2.3.1 If GPC cleanup of samples is required because of poor GC/EC chromatography in analysis, dilute the extract to 10 mL with methylene chloride and perform GPC cleanup as per Section 6.2.3. The reagent blank accompanying the samples should be included, unless only one or a partial group of samples requires cleanup. In this case, set up a new reagent blank with 10 mL of methylene chloride and appropriate surrogate standard added.

6.2.4 Concentrate the extract as per Sections 6.1.7 and 6.1.8.

6.3 Final Concentration of Extract with Optional Extract Splitting Procedure

If the extract in Section 6.1.8 is to be used only for pesticide/PCB analysis, it must be concentrated to a volume of 1.0 mL, following the procedure in Section 6.3.1.

If the extract in Section 6.1.8 is to be used for both semivolatile and pesticide/PCB analyses, then it must be split into two portions. In that case, follow the procedure in Section 6.3.1 to obtain the pesticide portion, and follow that with the procedure in Section 6.3.2 to obtain the semivolatile portion. Refer to the semivolatile methods for specific instructions regarding the treatment of extracts for semivolatile analysis.

6.3.1 If the extract is to be used only for the pesticide/PCB analysis, or if the same extract is used for both semivolatile and pesticide/PCB analyses to split out the pesticide/PCB extract, transfer 0.5 mL of the 10-mL methylene chloride extract to a separate concentrator tube. Add 5 mL of hexane and a silicon carbide boiling chip and mix using vortex mixer. Attach a two-ball micro-Snyder column. Pre-wet the Snyder column by adding 0.5 mL of hexane to the top of the column. Place the K-D apparatus on a hot water bath (80 to 90°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 min. Concentrate the extract to an apparent volume of less than 1 mL. Use nitrogen blowdown (Section 6.3.3) to reduce the volume to 0.5 mL. Add 0.5 mL of acetone. The pesticide extract must now be passed through an alumina column to remove the base/neutral and acid surrogates and polar interferencs. Proceed to Section 6.4.

6.3.2 If the extract in Section 6.1.8 was split in Section 6.3.1 to obtain a portion for pesticides analysis, the portion for semivolatile analysis must be treated according to the procedures in the semivolatile methods.

6.3.3 Nitrogen blowdown technique. Place the concentrator tube in a warm water bath (35°C) and evaporate the solvent volume to below 1 mL using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon). Caution: New plastic tubing must not be used between the carbon trap and the sample, since it may introduce interferences.

The internal wall of the tube must be rinsed down several times with hexane during the operation. During evaporation, the tube solvent level must be kept below the water level of the bath. The extract must never be allowed to become dry. If GPC cleanup techniques were employed, the 0.5-mL volume represents a twofold dilution to account for the fact that only half the extract went through the GPC.

6.3.4 Store all extracts at 4°C (±2°C) in the dark in Teflon-sealed containers until all analyses are performed.

6.4 Alumina Column Cleanup

All samples prepared from the same extract as used for the semivolatile analysis must be taken through this cleanup technique to eliminate BNA surrogates that will interfere in the GC/EC analysis.

6.4.1 Add 3 g of activity III neutral alumina to the 10-mL chromatographic column. Tap the column to settle the alumina. Do not pre-wet the alumina.

6.4.2 Transfer the 1.0 mL of hexane/acetone extract from Section 6.3.1 to the top of the alumina using a disposable Pasteur pipet. Collect the eluate in a clean, 10-mL concentrator tube.

6.4.3 Add 1 mL of hexane to the original extract concentrator tube to rinse it. Transfer these rinsings to the alumina column. Elute the column with an additional 9 mL of hexane. Do not allow the column to go dry during the addition and elution of the sample.

6.4.4 Concentrate the extract to 1.0 mL following either Section 6.3.1 or 6.3.3, using hexane where methylene chloride is specified. When concentrating medium level extracts, the nitrogen blowdown technique should be used to avoid contaminating the micro-Snyder column.

6.4.5 Observe the appearance of the extract.

6.4.5.1 If crystals of sulfur are evident or sulfur is expected to be present, proceed to Section 6.5.

6.4.5.2 If the sulfur is not expected to be a problem, transfer the 1.0-mL extract to a GC vial and label as pesticide/PCB fraction. The extract is ready for GC/EC analysis. Store the extracts at 4°C (±2°C) in the dark until analyses are performed.

6.5 Optional Sulfur Cleanup

6.5.1 Transfer the 1.0 mL from Section 6.4.5 to a 50-mL clear glass bottle or vial with a Teflon-lined screw cap. Rinse the concentrator tube with 1.0 mL of hexane, adding the rinsings to the 50-mL bottle. If only a partial set of samples requires sulfur cleanup, set up a new reagent blank with 1.0 mL of hexane and take it through the sulfur cleanup. Include the surrogate standards.

6.5.2 Add 1 mL of TBA-sulfite reagent and 1 mL of 2-propanol, cap bottle, and shake the bottle for at least 1 min. If the sample is colorless or if the initial color is unchanged, and if clear crystals (precipitated sodium sulfite) are observed, sufficient sodium sulfite is present. If the precipitated sodium sulfite disappears, add more crystalline sodium sulfite in approximately 100-mg portions until a solid residue remains after repeated shaking.

6.5.3 Add 5 mL of distilled water and shake for at least 1 min. Allow the sample to stand for 5 to 10 min and remove the hexane layer (top) for analysis. Concentrate the hexane to 10 mL as per Sections 6.3.1 and 6.3.3 using hexane where methylene chloride is specified. The temperature for the water bath should be about 80°C for the micro-Snyder column technique. Continue as outlined in Section 6.4.5.2.

GC/EC ANALYSIS OF PESTICIDES/PCBs

1.0 SUMMARY OF METHOD

1.1 The hexane extracts of water and soil/sediment are analyzed on a gas chromatograph/electron capture detector (GC/EC). If pesticides or PCBs are tentatively identified, a second GC/EC analysis is required using an alternate column. Quantitation must be on a packed column, whereas, confirmation can be on either a packed or a capillary column.

2.0 INTERFERENCES

2.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory method blanks.

3.0 APPARATUS AND EQUIPMENT

3.1 Gas chromatograph - An analytical system complete with gas chromatograph and all required accessories including syringes, analytical columns, gases, electron capture detector, and strip-chart recorder with recording integrator. A data system is required for measuring peak areas or peak heights and recording retention times. An electrolytic conductivity detector is also acceptable if the required quantitation limits are met. Overlapping peaks on chromatograms are not acceptable.

3.1.1 Quantitation and/or confirmation columns

3.1.1.1 Column 1 - Gas Chrom Q (100/120 mesh) or equivalent coated with 1.5 percent OV-17/1.95 percent OV-210 or equivalent packed in a 1.8-m long x 4-mm I.D. (6-mm O.D.) glass column.

Note: The 2mm-I.D. column cited in Table 1 as Column 1 will not adequately separate dibutylchlorendate and endrin ketone.

3.1.1.2 Column 2 - Gas Chrom Q (100/120 mesh) or equivalent coated with 3 percent OV-1 or equivalent packed in a 1.8-m long x 2-mm I.D. (6-mm O.D.) glass column.

3.1.1.3 Column 3 - Gas Chrom Q (80/100 mesh) or equivalent coated with 5 percent OV-210 or equivalent packed in a 1.8-m long x 2-mm I.D. (6-mm O.D.) glass column.

3.1.2 Confirmation column only. Column - 30-m x 0.25-mm I.D., 0.25-u film thickness, bonded-phase silicone coated, fused silica capillary column (J&W Scientific DB-5 or DB-1701 or equivalent). Note: DB-1701 provides better separation of pesticide method parameters. Column - 10-m x 0.32-mm I.D., 1-u film thickness has been used.

3.2 Balance - Analytical, capable of accurately weighing ±0.0001 g.

4.0 REAGENTS

4.1 Isooctane (2,2,4-trimethylpentane), hexane, and toluene - Pesticide quality or equivalent.

4.2 Stock standard solutions (1.00 ug/uL) - Stock standard solution can be prepared from pure standard materials or purchased as certified solutions.

4.2.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in toluene, dilute to volume in a 10-mL volumetric flask with isooctane. Larger volumes can be used at the convenience of

6.2.3 Determine if any pesticides/PCBs listed in Table D-3 are present. Pattern recognition techniques, based on chromatograms of standards, are recommended for the identification of PCB compounds.

6.2.3.1 If the response for any of these compounds is 100 percent or less of full scale, the extract is ready for confirmation and quantitation.

6.2.3.2 If the response for any compound is greater than full scale, dilute the extract so that the peak will be between 50 and 100 percent full scale and re-analyze on the packed column. Use this dilution also for confirmation and quantitation.

6.2.3.3 For dilution greater than tenfold. Also inject an aliquot of a dilution tenfold more concentrated to determine if other compounds of interest are present at lower concentrations.

6.2.3.4 Computer reproductions of chromatographs manipulated to ensure all peaks are on scale over a 100-fold range are an accepted substitute. However, this can be no greater than a 100-fold range. This is to prevent retention time shifts by column or detector overload. Linearity must be demonstrated over the 100-fold range using higher concentrations of the evaluation mixture.

6.2.4 Quantitation may be performed on the primary analysis, with the exception of toxaphene and possibly the DDT series. If DDT exceeds the 10.0 percent RSD linearity criterion, then quantitations for any DDE, DDD, and DDT in a sample must be on the confirmation analysis. Toxaphene must always be quantitated on the confirmation analysis. See Section 9.0 for special QC requirements for quantitation.

6.2.5 If identification of compounds of interest is prevented by the presence of interferences, further cleanup is required. If sulfur is evident, a sulfur cleanup is required. If unknown interferences or poor chromatography are noted only in the sample chromatogram, it is recommended that gel permeation chromatography cleanup be applied.

6.2.6 When selecting a GC column for confirmation and/or quantitation, be sure that none of the compounds to be confirmed/quantitated overlap; i.e., do not select the 3 percent OV-1 column if DDE and dieldrin are to be confirmed and/or quantitated. When samples are very complex, it may be necessary to use all three packed columns to achieve adequate separation ($\geq$25 percent resolution) of all compounds being quantitated.

7.0 GC/EC CONFIRMATION ANALYSIS

7.1 The purpose of confirmation analysis is to confirm the presence of all compounds tentatively identified in the Primary Analysis. Therefore, the only standards that are required are the Evaluation Standard Mixtures (to check linearity and degradation criteria) and standards of all compounds to be confirmed. The linearity criterion on the confirmation column for pesticides is not required unless the column is used for quantitation. The 72-h sequence in Section 6.1.3.5 is, therefore, modified to fit each case. Quantitation may be performed on the confirmation analysis. If toxaphene or DDT is to be quantitated, additional linearity requirements are specified in Section 7.3.1.

7.2 Table 1 provides examples of operating conditions for the gas chromatograph. Separation should be $\geq$25 percent resolution between peaks. Percent resolution is calculated by dividing the height of the valley by the peak height of the smaller peak being resolved, multiplied by 100. This criterion must be considered when determining whether to quantitate on the primary analysis or the confirmation analysis. When this criterion cannot be met, quantitation is adversely affected because of the difficulty in determining where to establish the baseline.

For a fused silica capillary column (FSCC) confirmation, there must be ≥25 percent resolution (valley) between the following pesticide pairs:

1. Beta-BHC and delta-BHC
2. Dieldrin and 4,4'-DDT
3. 4,4'-DDD and Endrin Aldehyde
4. Endosulfan Sulfate and 4,4'-DDT.

All QC requirements specified in Section 9.0 must be adhered to: i.e., the ≥12-min retention time for 4,4'-DDT, the criteria for 4,4'-DDT and endrin degradation, linearity, calibration factor for standards, and retention time shift for dibutylchlorendate. The retention time criterion for 4,4'-DDT does not have to be met if the confirmation column is OV-1 or OV-101. Apply instructions from Section 6.1.3 to the confirmation analysis.

7.3 Inject 2 to 5 uL (1 to 2 uL for capillary columns) of the sample extract and standards using the solvent-flush technique or autosamplers. A 1-uL volume can be injected only if automatic devices are employed. Record the volume injected to the nearest 0.05 uL and the total extract volume. The detector attenuation must provide peak response equivalent to the primary analysis response for each compound to be confirmed.

7.3.1 Begin the confirmation analysis GC sequence with the three concentration levels of Evaluation Standards Mixtures A, B, and C. The exception to this occurs when toxaphene and/or DDT series are to be confirmed and quantitated. There are four combinations of pesticides that could occur, therefore, the following sequences must be followed depending on the situation.

7.3.1.1 Toxaphene only - Begin the sequence with Evaluation Mixture B to check degradation, followed by three concentration levels of toxaphene. Check linearity by calculating percent relative standard deviation (%RSD).

If ≤10.0 %RSD, use the appropriate equation in Section 8.0 for calculation. If >10.0 %RSD, plot a standard curve and determine the ng for each sample in that set from the curve.

7.3.1.2 DDT, DDE, and DDD only - Begin the sequence with Evaluation Mixture B. Then inject three concentration levels of a standard containing DDE, DDD, and DDT. Calculate linearity and follow the requirements specified in Section 7.3.1.1 for each compound to be quantitated.

7.3.1.3 DDT series and toxaphene - Begin the sequence with Evaluation Mixture B. Then inject three concentration levels of toxaphene and another three levels of the DDT series. Calculate linearity and follow the requirements specified in Section 7.3.1.1 for each compound to be quantitated. Note: Capillary quantitation would be allowed only in this situation.

7.3.1.4 Other pesticides/PCBs plus DDT series and/or toxaphene - Begin the sequence with Evaluation Standard Mixtures A, B, and C. Calculate linearity on the four compounds in the Evaluation Standard Mixtures. If DDT and/or one or more of the other compounds are >10.0 %RSD and/or degradation exceeds the criterion, corrective maintenance as outlined in Section 9.0 should be performed before repeating the above chromatography evaluations. If only DDT exceeds the linearity criterion and one or more of the DDT series is to be quantitated, follow Section 7.3.1.2 (do not repeat Evaluation Mixture B).

If none of the DDT series is to be quantitated and DDT exceeds the 10.0 %RSD, simply record the %RSD on the proper form. Any time toxaphene is to be quantitated, follow Section 7.3.1.1.

7.3.2 After the linearity standards required in Section 7.3.1 are injected, continue the confirmation analysis sequence by injecting standards for all compounds tentatively identified in the primary analysis, to establish the 72-h retention time windows (see paragraph 6.1.1). Analyze all confirmation standards for a case at the beginning, at intervals specified in Section 7.3.3, and at the end. Any pesticide outside of its established retention time window requires immediate investigation and correction before continuing the analysis. The laboratory must re-analyze all samples which follow the standard that exceeds the criterion.

7.3.3 After injection of the appropriate standards (see Section 7.3.2), begin injection of samples. Analyze groups of five samples. Analyze Evaluation Mixture B after the first group of five samples. After the second group of five samples, analyze a standard pertaining to the samples in the preceding groups (i.e., substitute standards pertaining to the preceding samples for Individual Mixtures A or B in Section 6.1.3.5). Continue analyzing groups of five samples, alternately analyzing Evaluation Mixture B and standards pertaining to the preceding samples between groups of five samples. The alternating standard's calibration factors must be within 15.0 percent of each other if quantitation is performed. Deviations larger than 15.0 percent require the laboratory to repeat the analyses of samples which were analyzed after the standard that exceeded the criterion. The 15.0 percent criterion only pertains to compounds being quantitated.

If more than one standard is required to confirm all compounds tentatively identified in the primary analysis, alternate the standards with Evaluation Mixture B. Samples must also be repeated if the degradation of either DDT and/or endrin exceeds 20.0 percent on the intermittent Evaluation Standard Mixture B.

If the samples are split between two or more instruments, all standards and blanks pertaining to those samples must be analyzed on each instrument.

7.3.4 Inject the method blank (extracted with each set of samples) on every GC and GC column on which the samples are analyzed.

7.4 Evaluation of Chromatograms

7.4.1 A compound tentatively identified in the primary analysis is confirmed if the retention time from the confirmation analysis falls within the retention time window of a corresponding standard that was chromatographed on the same instrument within a 72-h period.

7.4.2 Quantitation should be performed on the packed column chromatogram (primary or confirmation) that provides the best separation from interfering peaks.

7.4.2.1 Quantitation of Chlordane - Because weathering and/or different formulations of chlordane usually modify the pattern exhibited by technical chlordane, this method is not appropriate for determining technical chlordane. Instead, standards for alpha chlordane and gamma chlordane are used for quantitation, and each isomer of chlordane is reported separately.

7.4.3 Computer reproductions of chromatograms that are attenuated to ensure all peaks are on scale over a 100-fold range are acceptable. However, this can be no greater than a 100-fold range. This is to prevent retention time shifts by column or detector overload. Also, peak response must be >25 percent of full scale deflection to allow visual pattern recognition of multicomponent compounds, and individual compounds must be visible.

7.4.4 If identification of compounds of interest is prevented by the presence of interferences, further cleanup is required. If sulfur is evident, perform a sulfur cleanup.

If unknown interferences or poor chromatography are noted only in the sample chromatogram, it is recommended that gel permeation chromatography cleanup be applied.

7.4.5 Calculate surrogate standard recovery on all samples, blanks, and spikes unless the surrogate was diluted out. Determine if recovery is within limits and report on Form II (Figures 1 and 2). See formula for calculation in Section 8.3.

7.4.6 If pesticide/PCB method parameters were identified in the unspiked sample from which the matrix spike and matrix spike duplicate were prepared, confirmation analysis is required for the matrix spike and matrix spike duplicate. If pesticide/PCB method parameters were not identified in the unspiked sample, confirmation of the matrix spike and matrix spike duplicate is not required. Calculate matrix spike duplicate recoveries and report on Form III (Figures 3 and 4).

8.0 CALCULATIONS

8.1 Calculate the concentration in the sample using the following equation for external standards. Response can be measured by the manual peak height technique or by automated peak height or peak area measurements from an integrator.

8.1.1 Water

$$\text{Concentration (ug/L)} = \frac{(A_x)(I_s)(V_t)}{(A_s)(V_i)V_s)}$$

where:

A_x = Response for the parameter to be measured

A_s = Response for the external standard

V_t = Volume of total extract (uL) (Take into account any dilutions.)

I_s = Amount of standard injected in nanograms (ng)

V_i = Volume of extract injected (uL)

V_s = Volume of water extracted (mL).

8.1.2 Sediment/Soil

$$\begin{array}{l}\text{Concentration (ug/kg)} \\ \text{(Dry weight basis)}\end{array} = \frac{(A_x)(I_s)(V_t)}{(A_s)(V_i)(W_s)(D)}$$

where:

A_x, I_s, A_s, V_i = Same as given above in Section 8.1.1

V_t = Volume of low level total extract (Use 20,000 uL or a factor of this when dilutions are made other than those accounted for below.)

1. 1/20 total extract taken for pesticide analysis (derived from 0.5 mL of 10-mL extract)

2. Final concentration to 1.0 mL for pesticide analysis,

- or -

V_t = Volume of medium level total extract (Use 10,000 uL or a factor of this when dilutions are made.)

$$D = \frac{100 - \text{Percent moisture}}{100}$$ (Percent moisture determined in sample preparation)

W_s = Weight of sample extracted (g).

8.2 For multicomponent mixtures (chlordane, toxaphene and PCBs), match retention times of peaks in the standards with peaks in the sample. Quantitate every identifiable peak (>50 percent of the total area must be used) unless height or peak area of each identified peak in the chromatogram. Calculate as total response in the sample versus total response in the standard.

8.3 Calculation for surrogate and matrix spike recoveries.

$$\text{Percent recovery} = \frac{Q_d}{Q_a} \times 100\%$$

where:

Q_d = Quantity determined by analysis

Q_a = Quantity added to sample.

Be sure all dilutions are taken into account. Soil/sediment has a 20-fold dilution factor built into the method when accounting for 1/20 of extract taken for pesticide analysis and final dilution to 1 mL.

8.4 Report results in ug/L or ug/kg without correction for recovery data.

8.5 GC/MS Confirmation of Pesticides

Any compounds confirmed by two columns must also be confirmed by GC/MS if the concentration is sufficient for detection by GC/MS as determined by the laboratory generated detection limits.

8.5.1 The GC/MS would normally require a minimum concentration of 10 ng/uL in the final extract, for each single component compound.

8.5.2 The pesticide extract and associated blank should be analyzed by GC/MS as per the method "GC/MS Analysis of Semivolatiles."

8.5.3 The confirmation may be from the GC/MS analysis of the semivolatile extracts (sample and blank). However, if the compounds are not detected in the semivolatile extract even though the concentration is high enough, a GC/MS analysis of the pesticide extract is required.

8.5.4 A reference standard for the compound must also be analyzed by GC/MS. The concentration of the reference standard must be at a level that would demonstrate the ability to confirm the pesticides/PCBs identified by GC/EC.

8.5.5 In the event the GC/MS does not confirm the presence of the pesticides/PCBs identified by GC/EC, those compounds should be reported as not detected. The minimum quantitation limits should be adjusted to reflect the interferences. The inability to confirm the compounds by GC/MS should be documented.

8.5.6 For GC/MS confirmation of multichannel pesticides and PCBs, required deliverables are spectra of three major peaks of multicomponent compounds from samples and standards.

8.5.7 Quantitation by GC/MS must use the characteristic quantitation ions for pesticides/PCBs given in the method "GC/MS Analysis of Semivolatiles."

9.0 QUALITY ASSURANCE/QUALITY CONTROL

9.1 Method Blank Analysis

A method blank is a volume of deionized, distilled laboratory water for water samples, or a purified solid matrix for soil/sediment samples, carried through the entire analytical scheme (extraction, concentration, and analysis). For soil/sediment samples, a solid matrix suitable for pesticide analyses is available from EMSL-LV. The method blank volume or weight must be approximately equal to the sample volumes or sample weights being processed.

9.1.1 Method blank analysis must be performed at the following frequency for the analysis of pesticide/PCB method parameters:

1. Each Case, or

2. Each 14-calendar-day period during which samples in a Case are received (said period beginning with the receipt of the first sample in that Sample Delivery Group), or

3. Each 20 samples in a Case that are of similar matrix (water or soil) or similar concentration (soil only), or

4. Whenever samples are extracted by the same procedure (separatory funnel or continuous extraction),

whichever is most frequent, on each GC/MS or GC system used to analyze samples.

9.1.2 It is the laboratory's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be minimized.

9.1.3 For the purposes of this protocol, an acceptable laboratory method blank must contain less than the contract required detection limit of any single pesticide/PCB Target Compound (Table D-3). If a laboratory method blank exceeds these criteria, the analyst must consider the analytical system to be out of control. The source of the contamination must be investigated and appropriate corrective measures be taken and documented before further sample analysis proceeds. All samples processed with a method blank that is out of control (i.e., contaminated) must be re-extracted and re-analyzed. Problems and solutions must be documented.

9.1.4 Report results of method blank analysis using Form I (Organic Analysis Data Sheet, Figure 5). In addition, the samples associated with each method blank must be summarized on Form IV (Method Blank Summary, Figure 6). Detailed instructions for the completion of these forms can be found in the CLP Statement of Work for Organics Analysis (October, 1986). All sample concentration data shall be reported as uncorrected for blanks.

9.2 Surrogate Spike Analysis

Surrogate standard determinations are performed on all samples and blanks. All samples and blanks are fortified with surrogate spiking compounds before purging or extraction in order to monitor preparation and analysis of samples.

9.2.1 Each sample, matrix spike, matrix spike duplicate, and blank is spiked with surrogate compounds prior to extraction. The surrogate spiking compounds shown in Table 2 are used to fortify each sample, matrix spike, matrix spike duplicate, and blank with the proper concentrations. Performance-based criteria are generated from laboratory results. Therefore, deviations from the spiking protocol will not be permitted.

Table 2. Surrogate Spiking Compound

	Amount in Sample Extract[a]		
Compound	Fraction	Water	Soil/Sediment
Dibutylchlorendate	Pesticide	0.1 ug	0.1 ug

a. At the time of injection, before any optional dilution.

9.2.2 Surrogate spike recovery must be evaluated by determining whether the concentration (measured as percent recovery) falls inside the advisory recovery limits listed in Table 3.

Table 3. Advisory Surrogate Spike Recovery Limits

Fraction	Surrogate Compound	Water	Soil/Sediment
Pesticide	Dibutylchlorendate	24-154[a]	(20-150)[a]

a. These limits are for advisory purposes only. They are not used to determine if a sample should be re-analyzed. When sufficient data become available, the U.S. EPA may set performance-based contract required windows.

9.2.3 Report surrogate recovery data for the following:

1. Method blank analysis
2. Sample analysis
3. Matrix spike/matrix spike duplicate analyses.

The surrogate spike recovery data is summarized on Form II (Surrogate Spike Percent Recovery Summary, Figures 1 and 2). Detailed instructions for the completion of Form II can be found in the CLP Statement of Work for Organics Analysis.

9.3 Matrix Spike/Matrix Spike Duplicate Analysis (MS/MSD)

To evaluate the matrix effect of the sample upon the analytical methodology, the U.S. EPA has developed the following standard mixes to be used for matrix spike and matrix spike duplicate analyses.

Pesticides

Heptachlor
Aldrin
Dieldrin
Lindane
Endrin
4,4'-DDT

These compounds are subject to change depending upon availability and suitability for use as matrix spikes.

9.3.1 A matrix spike and matrix spike duplicate must be performed for each group of samples of a similar matrix, once:

1. Each Case of field samples received, or
2. Each 20 field samples in a Case, or
3. Each group of samples of a similar concentration level (soils only), or
4. Each 14-calendar-day period during which samples in a Case were received (said period beginning with the receipt of the first sample in that Sample Delivery Group),

whichever is most frequent.

9.3.2 Use the compounds listed in Section 9.3 to prepare matrix spiking solutions according to protocols described in the sample preparation methods. These methods stipulate the amount of matrix spiking solution to be added to the sample aliquots prior to extraction. Each method allows for optional dilution steps which must be accounted for when calculating percent recovery of the matrix spike and matrix spike duplicate samples.

9.3.2.1 Samples requiring optional dilutions and chosen as the matrix spike/matrix spike duplicate samples, must be analyzed at the same dilution as the original unspiked sample.

9.3.3 Individual component recoveries of the matrix spike are calculated using the following equation.

$$\text{Matrix spike percent recovery} = \frac{\text{SSR} - \text{SR}}{\text{SA}} \times 100$$

where:

SSR = Spike sample results

SR = Sample result

SA = Spike added from spiking mix.

9.3.4 The relative percent difference (RPD) between the matrix spike and matrix spike duplicate is calculated using the following equation.

$$RPD = \frac{D_1 - D_2}{(D_1 + D_2)/2} \times 100$$

where:

D_1 = First sample value

D_2 = Second sample value (duplicate).

9.3.5 The matrix spike results (concentrations) for nonspiked pesticide/PCB method parameters shall be reported on Form I (Organic Analysis Data Sheet, Figure 5) and the matrix spike percent recoveries shall be summarized on Form III (MS/MSD Recovery, Figures 3 and 4). These values will be used by EPA to periodically update existing performance-based QC recovery limits (Table 4).

The results for nonspiked pesticide/PCB method parameters in the matrix spike duplicate analysis shall be reported on Form I (Organic Analysis Data Sheet, Figure 5) and the percent recovery and the relative percent difference shall be summarized on Form III (MS/MSD Recovery, Figures 3 and 4). The RPD data will be used by the EPA to evaluate the long-term precision of the analytical method. Detailed instructions for the completion of Form III can be found in the CLP Statement of Work for Organics Analysis.

Table 4. Matrix Spike Recovery Limits[a]

Fraction	Matrix Spike Compound	Water	Soil/Sediment
Pesticide	Lindane	56-123	46-127
Pesticide	Heptachlor	40-131	35-130
Pesticide	Aldrin	40-120	34-132
Pesticide	Dieldrin	52-126	31-134
Pesticide	Endrin	56-121	42-139
Pesticide	4,4'-DDT	38-127	23-134

a. These limits are for advisory purposes only. They are not to be used to determine if a sample should be re-analyzed. When sufficient multi-lab data are available, standard limits will be calculated.

9.4 QC Requirements for Analysis

This section summarizes ongoing QC activities involved with pesticide/PCB analysis that were detailed in Sections 9.1, 9.2, and 9.3 and describes the additional QA/QC procedures required during the analysis of pesticide/PCBs that are not covered in Sections 9.1, 9.2, and 9.3.

9.4.1 The Contractor must perform the following:

1. Method blank analysis as per Section 9.1.

2. Spike all standards, samples, blanks, matrix spike and matrix spike duplicate samples with the surrogate spike compound (dibutylchlorendate) as per Section 9.2.

3. Matrix spike/matrix spike duplicate analysis as per Section 9.3.

9.4.2 The external standard quantitation method must be used to quantitate all pesticides/PCBs. Before performing any sample analysis, the laboratory is required to determine the retention time window for each pesticide/PCB method parameter and the surrogate spike compound, dibutylchlorendate. These retention time windows are used to make tentative identification of pesticides/PCBs during sample analysis.

9.4.2.1 Prior to establishing retention time windows, the GC operating conditions (oven temperature and flow rate) must be adjusted such that 4,4'-DDT has a retention time of $\geq$12 min on packed GC columns. Conditions listed in Table 1 may be used to achieve this criterion.

9.4.2.2 Establish retention time windows as follows.

9.4.2.2.1 At the beginning of the contract and each time a new GC column is installed, make three injections of all single component pesticides mixtures, multi-response pesticides, and PCBs throughout the course of a 72-h period. The concentration of each pesticide/PCB should be sufficient to provide a response that is approximately half scale. The three injections of each compound should be made at approximately equal intervals during the 72-h period (e.g., each compound should be injected near the beginning, near the middle, and near the end of the 72-h period).

9.4.2.2.2 Verify the retention time shift for dibutylchlorendate in each standard. The retention time shift between the initial and subsequent standards must be less than a 2.0 percent difference for packed columns (<0.3 percent for capillary column). If this criterion is not met, continue injecting replicate standards to meet this criterion.

9.4.2.2.3 Calculate the standard deviation of the three absolute retention times for each single component pesticide. For multi-response pesticides or PCBs, choose one major peak from the envelope and calculate the standard deviation of the three retention times for that peak.

9.4.2.2.4 The standard deviations determined in Section 9.4.2.2.3 shall be used to determine the retention time windows for a particular 72-h sequence. Apply plus or minus three times the standard deviations in Section 9.4.2.2.3 to the retention time of each pesticide/PCB determined for the first analysis of the pesticide/PCB standard in a given 72-h analytical sequence. This range of retention times defines the retention time window for the compound of interest for that 72-h sequence. Note that, by definition, the retention time of a pesticide/PCB from the first analysis of that compound in the 72-h sequence is the center of the retention time window. Do not use the retention time measured in Section 9.4.2.2.1 as the center of the retention time window. The experience of the analyst should weigh heavily in the interpretation of chromatograms. For multiresponse pesticide/PCBs, the analyst should utilize the retention time window but should relay primarily on pattern recognition.

For example, the three injections of aldrin in Section 9.4.2.2.1 have a mean retention time of 1.40 min and a standard deviation of 0.01 min. The retention time of the aldrin standard at the beginning the 72-h sequence begun today is 1.51 min. Three times the standard deviation (0.01) is applied to the retention time of aldrin from the sequence begun today; e.g., 1.51 + 3(0.01) = 1.48-1.54. If aldrin has a retention time of 1.60 min at the beginning of the next 72-h sequence, then the retention time window becomes 1.60 + 3(0.01) = 1.57 - 1.63 for that 72-h sequence.

9.4.2.2.5 In those cases where the retention time window for a particular pesticide/PCB is less than 0.01 min, the laboratory may substitute whichever of the following formulas apply.

1. For packed columns, the retention time window of the particular pesticide/PCB shall be calculated as ±1 percent of the initial retention time of the compound in the 72-h sequence.

2. For packed columns, the retention time window of the particular pesticide/PCB shall be calculated as +1 percent of the initial retention time of the compound in the 72-h sequence.

3. For capillary columns, the retention time window of the particular pesticide/PCB shall be calculated as ±0.15 percent of the initial retention time of the compound in the 72-h sequence.

9.4.2.2.6 Regardless of whether the retention time windows are calculated by the method in Section 9.4.2.2.4 or Section 9.4.2.2.5, the retention time windows must be reported as a range of values, not as, for example, 1.51 min ±1 percent.

9.4.2.2.7 The laboratory must calculate retention time windows for each pesticide/PCB on each GC column used at the beginning of the program and whenever a new GC column is installed. The data must be retained by the laboratory and made available during an on-site laboratory evaluation.

9.4.3 Primary GC Column Analysis

9.4.3.1 Primary analysis establishes whether or not pesticides/PCBs are present in the sample, and establishes a tentative identification of each compound. Quantitation may be performed on the primary analysis if the analysis meets all of the QC criteria specified for quantitation.

9.4.3.2 Separation should be $\geq$25 percent resolution between peaks. This criterion must be considered when determining whether to quantitate on the primary analysis or the confirmation analysis. When this criterion cannot be met, quantitation is adversely affected because of the difficulty in determining where to establish the baseline.

9.4.3.3 Evaluation Standard Mixtures

9.4.3.3.1 Prepare Evaluation Standard Mixtures A, B, and C (aldrin, endrin, 4,4'-DDT and dibutylchlorendate) at the three concentration levels described in Section 4.3.1. Analyze the three Evaluation Standard Mixtures sequentially at the beginning of each 72-h period (See Section 6.1.3.5).

9.4.3.3.2 Calculate the calibration factor (ratio of the total area to the mass injected) for each compound in Evaluation Standard Mixtures A, B and C using the following equation.

$$\text{Calibration factor} = \frac{\text{Total area of peak}}{\text{Mass injected (ng)}}$$

9.4.3.3.3 Using the calibration factors from Section 9.4.3.3.2 above, calculate the percent relative standard deviation (%RSD) for each compound at the three concentration levels using the following equation.

$$\% \text{ Relative Standard Deviation} = \frac{SD}{\bar{x}} \times 100$$

$$\text{Standard Deviation (SD)} = \sqrt{\sum_{i=1}^{N} \frac{(x_i - \bar{x})^2}{N-1}}$$

where:

$\bar{x}$ = Mean of initial three calibration factors (per compound).

The percent relative standard deviation for aldrin, endrin, and dibutylchlorendate must be <10.0 percent. If the %RSD exceeds 10.0 percent for 4,4'-DDT, see Section 9.4.5.4.4.

Note: The 10.0 %RSD linearity criteria pertains only to columns being used for pesticide/PCB quantitation. If a column is used only for surrogate quantitation, the 10.0 %RSD is only required for dibutylchlorendate.

9.4.3.3.4 Evaluate the chromatogram from the analysis of the Evaluation Mixture B. The appearance of peaks in addition to the four main pesticide peaks indicates a breakdown of endrin and/or 4,4'-DDT.

9.4.3.3.5 Calculate the percent breakdown for endrin and/or 4,4'-DDT on the mixed phase (1.5 percent OV-16/1.95 percent OV-210 or equivalent) GC column using the following equations. The percent breakdown for endrin or 4,4'-DDT must not exceed 20.0 percent. Corrrective action must be taken before analysis continues.

$$\text{Percent breakdown for 4,4'-DDT} = \frac{\text{Total DDT degradation peak area (DDE + DDD)}}{\text{Total DDT peak area (DDT + DDE + DDD)}} \times 100.$$

Percent breakdown for endrin =

$$\frac{\text{Total Endrin degradation peak areas (Endrin Aldehyde + Endrin Ketone)}}{\text{Total Endrin Peak Area (Endrin + Endrin Aldehyde + Endrin Ketone)}} \times 100.$$

9.4.3.3.6 Calculate the percent breakdown for endrin and/or 4,4'-DDT on the OV-1 or equivalent GC column using the above equations. The percent breakdown for endrin or 4,4'-DDT must not exceed 20.0 percent. Corrective action must be taken before analysis continues.

9.4.3.3.7 If there is evidence of a peak at the retention time for endrin aldehyde/4,4'-DDD (which coelute on the OV-1 or equivalent GC column), calculate a combined percent breakdown for endrin/4,4'-DDT using the following equation. The combined endrin/4,4'-DDT percent breakdown must not exceed 20.0 percent, else corrective action must be taken before analysis continues. Note: The term "peak height" may be substituted for the term "peak area."

Combined percent breakdown =

$$\frac{\text{Total Endrin/DDT degradation peak areas(DDD,DDE,Endrin Aldehyde+Endrin Ketone)}}{\text{Total Endrin/DDT peak area (Endrin,Endrin Aldehyde,Endrin Ketone, DDT,DDD,DDE)}}$$

9.4.3.8 Suggested Maintenance

Corrective measures may require any one or more of the following remedial actions:

1. Packed columns - For instruments with off-column injection, replace the demister trap, clean and deactivate the glass injection port, and insert or replace with a cleaned and deactivated insert. Inspect the injection end of the column and remove any foreign material (broken glass from the rim of the column or pieces of septa). Replace the glass wool with fresh deactivated glass wool. Also, it may be necessary to remove the first few millimeters of packing material if any discoloration is noted. Also swab out the inside walls of the column if any residue is noted. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body (described below) and/or repack/replace the column.

2. Capillary columns - Clean and deactivate the glass injection port insert or replace with a cleaned and deactivated insert. Break off the first few inches, up to one foot, of the injection port side of the column. Remove the column and solvent backflush according to the manufacturer's instructions. If these procedures fail

to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the column.

3. Metal Injector Body - Turn off the oven and remove the analytical column when the oven has cooled. Remove the glass injection port insert (instruments with off-column injection or Grob). Lower the injection port temperature to room temperature. Inspect the injection port and remove any noticeable foreign material.

4. Place a beaker beneath the injector port inside the GC oven. Using a wash bottle, serially rinse the entire inside of the injector port with acetone and then toluene, catching the rinsate in the beaker.

5. Prepare a solution of deactivating agent (Sylon-CT or equivalent) following manufacturer's directions. After all metal surfaces inside the injector body have been thoroughly coated with the deactivation solution, serially rinse the injector body with toluene, methanol, acetone, and hexane. Reassemble the injector and replace the GC column.

9.4.3.4 Individual Standard Mixtures A and B

9.4.3.4.1 Prepare Individual Standard Mixtures A and B containing the single component pesticides. These may be divided into the groups suggested in Section 6.1.4, which are recommended to prevent overlap of compounds on two of the packed columns. One mixture of all the single component pesticides is acceptable when using capillary column. Prepare separate solutions of all multi-response pesticides and PCBs. (Aroclor 1016 and Aroclor 1260 may be combined in a single mixture.)

9.4.3.4.2 Analyze Individual Standard Mixtures A and B and all multi-response pesticide/ PCBs at the beginning of each 72-h period (see Section 6.1.3.5) and analyze Individual Standard Mixtures A and B at the intervals specified in the analytical sequence in Section 6.1.3.5, and whenever sample analysis is completed. The calibration factor for each standard quantitated (Individual Standard Mixture A or B), must not exceed a 15.0 percent difference for a quantitation run nor exceed a 20.0 percent difference for a confirmation run during the 72-h period. Deviations greater than 15.0 percent require the laboratory to repeat the samples analyzed following the quantitation standard that exceeded the criterion.

Note: Aroclors 1221 and 1232 must be analyzed at a minimum of once a month on each instrument and each column. Copies of these chromatograms must be submitted with each case for instruments and columns used to quantitate samples in that case, when identity of these two pesticides (Aroclor 1221 and 1232) has been confirmed.

$$\text{Calibration factor} = \frac{\text{Total area of peak*}}{\text{Mass injected (ng)}}.$$

* For multiresponse pesticides/PCBs, use the total area of all peaks used for quantitation.

$$\text{Percent difference} = \frac{|R_1 - R_2|}{R_1} \times 100$$

where:

R_1 = Calibration factor from first analysis

R_2 = Calibration factor from second or subsequent analysis.

9.4.4 Sample Analysis (Primary GC Column)

9.4.4.1 Samples are analyzed per the sequence described in Section 6.1.3.5.

9.4.4.2 The retention time shift for dibutylchlorendate must be evaluated after the analysis of each sample. The retention time shift may not exceed a 2.0-percent difference for packed GC columns between the initial standard analysis and any sample or standard analyzed during the 72-h period. The percent difference for capillary columns must not exceed 0.3 percent.

$$\text{Percent difference (\%D)} = \frac{|RT_I - RT_S|}{RT_I} \times 100$$

where:

RT_I = Absolute retention time of dibutylchlorendate in the initial standard (Evaluation Standard Mixture A)

RT_S = Absolute retention time of dibutylchlorendate in the sample or subsequent standard.

9.4.4.3 Evaluate the GC column throughout the analysis of samples by injecting Evaluation Standard Mixture B at the frequency outlined in Section 6.1.3.5.

9.4.4.4 Calculate the percent breakdown for 4,4'-DDT and endrin according to Section 8.3. Take corrective action when the breakdown for 4,4'-DDT or endrin exceeds 20.0 percent.

9.4.4.5 If one or more compounds have a response greater than full scale, the extract requires dilution according to the specifications in Section 6.2.3. If the dilution of the extract causes any compounds tentatively identified in the first analysis to be undetectable in the second analysis, then the results of both analyses shall be reported on separate Forms I (Figure 5). For dilutions greater than tenfold, also see the instructions in Section 6.2.3.3.

9.4.5 Confirmation Analysis (GC/EC)

9.4.5.1 Confirmation analysis is to confirm the presence of all compounds tentatively identified in the primary analysis. Therefore, the only standards that are required are the Evaluation Standard Mixtures (to check linearity and degradation criteria) and standards of all compounds to be confirmed. The 72-h sequence described in Section 6.1.3.5 is, therefore, modified to fit each case. Quantitation may be performed on the confirmation analysis. If toxaphene or DDT is to be quantitated, additional linearity requirements are specified.

9.4.5.2 Separation should be $\geq$25 percent resolution betwe[illegible] peaks. This criterion must be considered when determining whether to quantitate on the primary analysis or the confirmation analysis. When this criterion cannot be met, quantitation is adversely affected because of the difficulty in determining where to establish the baseline.

For a fused silica capillary (FSCC) confirmation, there must be $\geq$25 percent resolution (valley) between the following pesticide pairs:

1. Beta-BHC and delta-BHC
2. Dieldrin and 4,4'-DDT
3. 4,4'-DDD and endrin aldehyde
4. Endosulfan Sulfate and 4,4'-DDT.

9.4.5.3 All QC-specified previously must be adhered to (i.e., the $\geq$12-min retention time for 4,4-DDT) and the specified criteria for 4,4'-DDT and endrin degradation, linearity, calibration factor for standards, and retention time shift for dibutylchlorendate. The retention time requirement for 4,4'-DDT does not have to be met if the confirmation column is OV-1 or OV-101.

9.4.5.4 Begin the confirmation analysis GC sequence with the three concentration levels of Evaluation Standard Mixtures A, B and C. The exception to this occurs when toxaphene and/or DDT series are to be confirmed and quantitated. There are four combinations of pesticides that could occur; therefore, the following sequences must be followed depending on the situation.

9.4.5.4.1 Toxaphene only - Begin the sequence with Evaluation Mixture B to check degradation, followed by three concentration levels to toxaphene. Check linearity by calculating %RSD. If <10.0 %RSD, use the appropriate equation in Section 8.0 for calculation. If >10.0 %RSD, plot a standard curve and determine the concentration for each sample in that set from the curve.

9.4.5.4.2 DDT, DDE, DDD only - Begin the sequence with Evaluation Mixture B. Then inject three concentration levels of a standard containing DDE, DDD and DDT. Calculate linearity and follow the requirements specified in 9.4.5.4.1 for each compound to be quantitated.

9.4.5.4.3 DDT series and toxaphene - Begin the sequence with Evaluation Mixture B. Then inject three concentration levels of toxaphene and another three levels of the DDT series. Calculate linearity and follow the requirements specified in 9.4.5.4.1 for each compound to be quantitated.

9.4.5.4.4 Other pesticides/PCBs plus DDT series and/or toxaphene - Begin the sequence with Evaluation Standard Mixtures A, B and C. Calculate linearity on the four compounds in the Evaluation Standards Mixtures. If DDT and/or one or more of the other compounds are >10.0 %RSD and/or degradation exceeds the criterion, corrective maintenance as outlined in paragraph 9.4.3.8 should be performed before repeating the above chromatography evaluations. If DDT only exceeds the linearity criteria and one or more of the DDT series is to be quantitated, follow 9.4.5.4.2 (do not repeat Evaluation Mixture B). If none of the DDT series is to be quantitated and DDT exceeds the 10.0 %RSD, simply record the %RSD on the proper form. Anytime toxaphene is to be quantitated, follow 9.4.5.4.1.

9.4.5.5 After the linearity standards required in 9.4.5.4 are injected, continue the confirmation analysis injection sequence with all compounds tentatively identified during primary analysis to establish the daily retention time windows during primary analysis. Analyze all confirmation standards for a case at the beginning, at intervals specified in 9.4.5.6, and at the end. Any pesticide outside of its established retention time window requires immediate investigation and correction before continuing the analysis. The laboratory must reanalyze all samples between the standard that exceeds the criterion and a subsequent standard that meets the criterion.

9.4.5.6 Begin injection of samples at this point of the Confirmation Analysis sequence. Analyze groups of 5 samples with a standard pertaining to the samples after each group (Evaluation Mixture B is required after the first 5 samples, and every 10 samples thereafter, e.g., after 5, 15, 25, etc.). The alternating standard's calibration factors must be within 15.0 percent of each other if quantitation is performed. Deviations larger than 15.0 percent require the laboratory to repeat the samples analyzed between the standard that exceeds the criterion and a subsequent standard that meets the criterion. The 15.0 percent criterion only pertains to compounds being quantitated.

1. If more than one standard is required to confirm all compounds tentatively identified in the primary analysis, include an alternate standard after each 10 samples.

2. Samples must also be repeated if the degradation of either DDT and/or endrin exceeds 20.0 percent on the intermittent Evaluation Standard Mixture B.

3. If the samples are split between 2 or more instruments, all standards and blanks pertaining to those samples must be analyzed on each instrument.

9.4.5.7 Inject the method blanks (extracted with each set of samples) on every GC and GC column on which the samples are analyzed.

9.4.5.8 If quantitation is performed on the confirmation analysis, follow the instructions in 9.4.4.5 regarding dilution of extracts and reporting results.

9.4.6 GC/MS Confirmation of Pesticide/PCB

9.4.6.1 Any pesticide/PCB confirmed by two dissimilar GC columns must also be confirmed by GC/MS if the concentration in the final sample extract is sufficient for GC/MS analysis (based on laboratory GC/MS detection limits).

Pesticides/PCBs may be confirmed utilizing the extract prepared for semivolatile GC/MS analysis; however, the absence of pesticide/PCBs in the semivolatile extract would require the analysis of the pesticide/PCB (fraction) extract.

9.4.6.2 The tuning and mass calibration criteria for DFTPP (50 ng) must be met before any confirmation of pesticides/PCBs is undertaken. Refer to the tuning and mass calibration instruction for semivolatiles. The characteristic ions for GC/MS analysis of pesticides/PCBs are given in the method UGC/MS Analysis of Semivolatiles.

9.4.6.3 The pesticide/PCB sample extract(s) and the associated pesticide/PCB blank(s), and reference standard(s) must be analyzed by GC/MS.

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SOIL PESTICIDE SURROGATE RECOVERY

Lab Name: ______________________ Contract: ____________

Lab Code: ________ Case No.: ______ SAS No.: ______ SDG No.: _____

Level: (low/med) ________

	EPA SAMPLE NO.	S1 (DBC)#	OTHER
01			
02			
03			
04			
05			
06			
07			
08			
09			
10			
11			
12			
13			
14			
15			
16			
17			
18			
19			
20			
21			
22			
23			
24			
25			
26			
27			
28			
29			
30			

S1 (DBC) = Dibutylchlorendate

ADVISORY
QC LIMITS
(24-154)

# Column to be used to flag recovery values with an asterisk

*Values outside of QC limits

Page ___ of ___ FORM II PEST-2 10/86

Figure 1. Soil Pesticide Surrogate Recovery

WATER PESTICIDE SURROGATE RECOVERY

Lab Name: ____________________ Contract: __________
Lab Code: ________ Case No.: ________ SAS No.: ______ SDG No.: ______

	EPA SAMPLE NO.	S1 (DBC) #	OTHER
01			
02			
03			
04			
05			
06			
07			
08			
09			
10			
11			
12			
13			
14			
15			
16			
17			
18			
19			
20			
21			
22			
23			
24			
25			
26			
27			
28			
29			
30			

ADVISORY
QC LIMITS
S1 (DBC) = Dibutylchlorendate (20-150)

# Column to be used to flag recovery values with an asterisk

*Values outside of QC limits

Page ___ of ___ FORM II PEST-1 10/86

Figure 2. Water Pesticide Surrogate Recovery

SOIL PESTICIDE MATRIX SPIKE/MATRIX SPIKE DUPLICATE RECOVERY

Lab Name: ____________________ Contract: __________
Lab Code: ______ Case No.: ______ SAS No.: ______ SDG No.: ______
Matrix Spike - EPA Sample No.: ______ Level: (low/med) ______

COMPOUND	AMOUNT ADDED (ng)	SAMPLE CONC. IN EXTRACT (ug/L)	MS CONC. IN EXTRACT (ug/L)	MS% REC #	QC LIMITS REC.
Lindane					46-127
Heptachlor					35-130
Aldrin					34-132
Dieldrin					31-134
Endrin					42-139
4,4'-DDT					23-134

COMPOUND	MSD CONC. IN EXTRACT (ug/L)	MSD% REC #	MS% REC #	% RPD #	QC LIMITS	
					RPD	REC.
Lindane					50	46-127
Heptachlor					31	35-130
Aldrin					43	34-132
Dieldrin					38	31-134
Endrin					45	42-139
4,4'-DDT					50	23-134

Column to be used to flag recovery and RPD values with an asterisk
*Values outside of QC limits

RPD: ______ out of ______ outside limits
Spike Recovery: ______ out of ______ outside limits

COMMENTS: ____

FORM III PEST-1 10/86

Figure 3. Soil Pesticide MS/MSD Recovery

WATER PESTICIDE MATRIX SPIKE/MATRIX SPIKE DUPLICATE RECOVERY

Lab Name: ____________________ Contract: ____________
Lab Code: ________ Case No.: ______ SAS No.: ______ SDG No.: ______
Matrix Spike - EPA Sample No.: __________

COMPOUND	AMOUNT ADDED (ng)	SAMPLE CONC. IN EXTRACT (ug/L)	MS CONC. IN EXTRACT (ug/L)	MS% REC #	QC LIMITS REC.
Lindane					56-123
Heptachlor					40-131
Aldrin					40-120
Dieldrin					52-126
Endrin					56-121
4,4'-DDT					38-127

COMPOUND	MSD CONC. IN EXTRACT (ug/L)	MSD% REC #	MS% REC #	% RPD #	QC LIMITS RPD	QC LIMITS REC.
Lindane					15	56-123
Heptachlor					20	40-131
Aldrin					22	40-120
Dieldrin					18	52-126
Endrin					21	56-121
4,4'-DDT					27	38-127

# Column to be used to flag recovery and RPD values with an asterisk
*Values outside of QC limits

RPD: ______ out of ______ outside limits
Spike Recovery: ______ out of ______ outside limits

COMMENTS: ____

FORM III PEST-1 10/86

Figure 4. Water Pesticide MS/MSD Recovery

PESTICIDE ORGANICS ANALYSIS DATA SHEET

EPA SAMPLE NO. ______

Lab Name: ______ Contract: ______
Lab Code: ______ Case No.: ______ SAS No.: ______ SDG No.: ______
Matrix: (soil/water) ______ Lab Sample ID: ______
Sample wt/vol: ______ (g/mL) ______ Lab File ID: ______
Level: (low/med) ______ Date Received: ______
% Moisture: not dec. ______ dec. ______ Date Extracted: ______
Extraction: (SepF/Cont/Sonc) ______ Date Analyzed: ______
GPC Cleanup: (Y/N) ______ pH: ______ Dilution Factor: ______

CAS NO.	COMPOUND	CONCENTRATION UNITS: (ug/L or ug/Kg)______	Q
319-84-6	alpha-BHC		
319-85-7	beta-BHC		
319-86-8	delta-BHC		
58-89-9	gamma-BHC (Lindane)		
76-44-8	Heptachlor		
309-00-2	Aldrin		
1024-57-3	Heptachlor epoxide		
959-98-8	Endosulfan I		
60-57-1	Dieldrin		
72-55-9	4,4'-DDE		
72-20-8	Endrin		
33213-65-9	Endosulfan II		
72-54-8	4,4'-DDD		
1031-07-8	Endosulfan sulfate		
50-29-3	4,4'-DDT		
72-43-5	Methoxychlor		
53494-70-5	Endrin ketone		
5103-71-9	alpha-Chlordane		
5103-74-2	gamma-Chlordane		
8001-35-2	Toxaphene		
12674-11-2	Aroclor-1016		
11104-28-2	Aroclor-1221		
11141-16-5	Aroclor-1232		
53469-22-9	Aroclor-1242		
12672-29-6	Aroclor-1248		
11097-69-1	Aroclor-1254		
11096-82-5	Aroclor-1260		

FORM I PEST 10/86

Figure 5. Pesticide Organics Analysis Data Sheet

PESTICIDE METHOD BLANK SUMMARY

Lab Name: ____________________ Contract: __________
Lab Code: ________ Case No.: ______ SAS No.: ______ SDG No.: ______
EPA Sample No. for Method Blank: ________ Lab Sample ID: ________
Instrument ID: __________ Lab File ID: ________
Date Extracted: __________ Extraction: (SepF/Cont/Sonc) ______
Date Analyzed (1): __________ Date Analyzed (2): __________
Time Analyzed (1): __________ Time Analyzed (2): __________
Instrument ID (1): __________ Instrument ID (2): __________
GC Column ID (1): __________ GC Column ID (2): __________

THIS METHOD BLANK APPLIES TO THE FOLLOWING SAMPLES, MS AND MSD:

	EPA SAMPLE NO.	LAB SAMPLE ID (1)	DATE ANALYZED (1)	LAB SAMPLE ID (2)	DATE ANALYZED (2)
01					
02					
03					
04					
05					
06					
07					
08					
09					
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					
21					
22					
23					
24					
25					

COMMENTS: ____
____
____

Page ___ of ___ FORM IV PEST 10/86

Figure 6. Pesticide Method Blank Summary

PESTICIDE EVALUATION STANDARDS SUMMARY

Lab Name: ____________________ Contract: __________
Lab Code: ______ Case No.: ______ SAS No.: ______ SDG No.: ______
Instrument ID: ________ GC Column ID: ____________
Dates of Analyses: ______ to ______

Evaluation Check for Linearity

LAB SAMPLE ID (STANDARD)	______	______	______	______
PESTICIDE	CALIBRATION FACTOR EVAL MIX A	CALIBRATION FACTOR EVAL MIX B	CALIBRATION FACTOR EVAL MIX C	% RSD (>/= 10.0%)
ALDRIN				
ENDRIN				
4,4'-DDT				(1)
DIBUTYL CHLORENDATE				

(1) If > 10.0% RSD, plot a standard curve and determine the ng for each sample in that set from the curve.

Evaluation Check for 4,4'-DDT/Endrin Breakdown
(percent breakdown expressed as total degradation)

	LAB SAMPLE ID (STANDARD)	TIME OF ANALYSIS	ENDRIN	4,4'-DDT	COMBINED
01 INITIAL EVAL MIX B					
02 EVAL MIX B					
03 EVAL MIX B					
04 EVAL MIX B					
05 EVAL MIX B					
06 EVAL MIX B					
07 EVAL MIX B					
08 EVAL MIX B					
09 EVAL MIX B					
10 EVAL MIX B					
11 EVAL MIX B					
12 EVAL MIX B					
13 EVAL MIX B					
14 EVAL MIX B					

Page ___ of ___ FORM VIII PEST-1 10/86

Figure 7. Pesticide Evaluation Standards Summary

PESTICIDE EVALUATION STANDARDS SUMMARY
Evaluation of Retention Time Shift for Dibutylchlorendate

Lab Name: ____________________ Contract: ____________
Lab Code: ________ Case No.: ______ SAS No.: ______ SDG No.: ______
Instrument ID: __________ GC Column ID (2) ______________
Dates Analyses: _____ to ______

	EPA SAMPLE NO.	LAB SAMPLE ID	DATE OF ANALYSIS	TIME OF ANALYSIS	% D	*
01						
02						
03						
04						
05						
06						
07						
08						
09						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						
26						
27						
28						
29						
30						
31						
32						
33						
34						
35						
36						
37						
38						

*Values outside of QC limits (2.0% for packed columns, 0.3% for capillary columns)

Page ___ of ___

FORM VIII PEST-2 10/

Figure 8. Pesticide Evaluation Standards Summary, Evaluation of Retention Time Shift for Dibutylchlorendate

PESTICIDE/PCB STANDARDS SUMMARY

Lab Name: ______________ Contract: ______________
Lab Code: ________ Case No.: ________ SAS No.: ________ SDG No.: ________
Instrument ID: ________ GC Column ID: ________

	DATE(S) OF ANALYSIS FROM: ______ TO: ______ TIME(S) OF ANALYSIS FROM: ______ TO: ______				DATE OF ANALYSIS ______ TIME OF ANALYSIS ______ LAB SAMPLE ID (STANDARD) ______			
COMPOUND	RT	RT WINDOW		CALIBRATION FACTOR	RT	CALIBRATION FACTOR	QNT Y/N	%D
		FROM	TO					
alpha-BHC								
beta-BHC								
delta-BHC								
Heptachlor								
Aldrin								
Hept. Epoxide								
Endosulfan I								
Dieldrin								
4,4'-DDE								
Endrin								
Endosulfan II								
4,4'-DDD								
Endo.Sulfate								
4,4'-DDT								
Methoxychlor								
Endrin Ketone								
a.Chlordane								
g.Chlordane								
Toxaphene								
Aroclor-1016								
Aroclor-1221								
Aroclor-1232								
Aroclor-1242								
Aroclor-1248								
Aroclor-1254								
Aroclor-1260								

Under QNT Y/N: enter Y if quantitation was performed, N if not performed. %D must be less than or equal to 15.0% for quantitation, and less than or equal to 20.0% for confirmation.

Note: Determining that no compounds were found above the CRDL is a form of quantitation, and therefore at least one column must meet the 15.0% criteria.

For multicomponent analytes, the single largest peak that is characteristic of the component should be used to establish retention time and %D. Identification of such analytes is based primarily on pattern recognition.

Page ___ of ___ FORM IX PEST 10/86

Figure 9. Pesticide/PCB Standards Summary

PESTICIDE/PCB IDENTIFICATION

EPA SAMPLE NO.

____

Lab Name: __________ Contract: __________
Lab Code: ______ Case No.: ______ SAS No.: ______ SDG No.: ______
GC Column ID (1): ______ GC Column ID (2) : ______
Instrument ID (1): ______ Instrument ID (2): ______
Lab Sample ID (1): ______ Lab Sample ID (2): ______
Lab File ID: ______ (only if confirmed by GC/MS)

	PESTICIDE/PCB	RETENTION TIME	RT WINDOW OF STANDARD FROM	TO	QUANT? (Y/N)	GC/MS? (Y/N)
01	______	Column 1____	____	____	____	____
02		Column 2____	____	____	____	____
03	______	Column 1____	____	____	____	____
04		Column 2____	____	____	____	____
05	______	Column 1____	____	____	____	____
06		Column 2____	____	____	____	____
07	______	Column 1____	____	____	____	____
08		Column 2____	____	____	____	____
09	______	Column 1____	____	____	____	____
10		Column 2____	____	____	____	____
11	______	Column 1____	____	____	____	____
12		Column 2____	____	____	____	____

Comments: __________

Page __ of __ FORM X PEST 10/86

Figure 10. Pesticide/PCB Identification

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INORGANIC
ANALYSIS METHODS

DETERMINATION OF METALS BY INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY

1.0 SCOPE AND APPLICATION

1.1 This inductively coupled plasma-atomic emission spectrometric (ICP) method incorporates the sample preparation, analysis, and reporting forms for the ICP portion of the determination of U.S. Environmental Protection Agency (EPA) Contract Laboratory Program (CLP) metals and for the ICP Method for the DOE Environmental Survey. The sample preparation is common to both determinations. But, the method detection levels (MDL) for the Survey ICP Method and contract required detection levels (CRDL) for the CLP protocol differ (see Table 1) in that the CLP method requires the use of furnace atomic absorption (AA) to achieve the CRDLs for elements such as arsenic, lead, selenium, thallium, and possibly antimony, cadmium, and silver; while the Survey ICP method determines these elements to MDLs that are consistent with ICP instrument detection limits (IDL). The reporting forms are common to both methods.

1.2 Dissolved elements are determined in filtered and acidified samples. Appropriate steps must be taken in all analyses to ensure that potential interferences are taken into account. This is especially true when dissolved solids exceed 1500 mg/L. (See Section 3.0.)

1.3 Total elements are determined after appropriate digestion procedures are performed. Since digestion techniques increase the dissolved solids content of the samples, appropriate steps must be taken to correct for potential interference effects. (See Section 3.0.)

1.4 Table 2 lists elements along with recommended wavelengths and typical estimated IDLs using conventional pneumatic nebulization. Actual working detection limits are sample dependent and as the sample matrix varies, these concentrations may also vary. In time, other elements may be added as more information becomes available, and as required.

1.5 Because of the differences between various makes and models of satisfactory instruments, no detailed instrumental operating instructions can be provided. Instead, the analyst is referred to the instructions provided by the manufacturer of the particular instrument.

2.0 SUMMARY OF METHOD

2.1 The method describes a technique for the simultaneous or sequential multi-element determination of trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic line emission spectra are produced by a radio-frequency ICP. The spectra are dispersed by a grating spectrometer and the intensities of the line are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in Section 3.1 (and tests for their presence as described in Section 3.2) should also be recognized and appropriate corrections made.

3.0 INTERFERENCES

3.1 Several types of interference effects may contribute to inaccuracies in the determination of trace elements. They can be summarized as follows:

3.1.1 Spectral interferences can be categorized as (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) background contribution from stray light from the line emission of high concentration elements. The first of these effects can be compensated by utilizing a computer correction of the raw data, requiring the monitoring and measurement of the interfering element. The second effect may require selection of an alternate wavelength. The third and fourth effects can usually be compensated by a background correction adjacent to the analyte line. In addition, users of simultaneous multi-element instrumentation must assume the responsibility of verifying the absence of spectral interference from an element that could occur in a sample but for which there is no channel in the instrument array. Listed in Table 3 are some interference effects for the recommended wavelengths given in Table 2. The data in Table 3 are intended for use only as a rudimentary guide for the indication of potential spectral interferences. For this purpose, linear relations between concentration and intensity for the analytes and the interferents can be assumed. The interference information, which was collected at the Ames Laboratory,* is expressed as analyte concentration equivalents (i.e., false analyte concentrations) arising from 100 mg/L of the interferent element. The suggested use of this information is as follows: assume that arsenic (at 193.696 nm) is to be determined in a sample containing approximately 10 mg/L of aluminum. According to Table 3, 100 mg/L of aluminum would yield a false signal for arsenic equivalent to approximately 1.3 mg/L. Therefore, 10 mg/L of aluminum would result in a false signal for arsenic equivalent to approximately 0.13 mg/L. The reader is cautioned that other analytical systems may exhibit somewhat different levels of interference than those shown in Table 3, and that the interference effects must be evaluated for each individual system. Only those interferents listed were investigated and the blank spaces in Table 3 indicate that measurable interferences were not observed from the interferent concentrations listed in Table 4. Generally, interferences were discernible if they produced peaks or background shifts corresponding to 2 to 5 percent of the peaks generated by the analyte concentrations also listed in Table 4.

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*Ames Laboratory, USDOE, Iowa State University, Ames, IA, 50011.

At present, information on the listed silver and potassium wavelengths is not available but it has been reported that second order energy from the magnesium 383.231-nm wavelength interferes with the listed potassium line at 766.491 nm.

3.1.2 Physical interferences are generally considered to be effects associated with the sample nebulization and transport processes. Such properties as change in viscosity and surface tension can cause significant inaccuracies especially in samples which may contain high dissolved solids and/or acid concentrations. The use of a peristaltic pump may lessen these interferences. If these types of interferences are operative, they must be reduced by dilution of the sample and/or acid concentrations. Another problem which can occur from high dissolved solids is salt buildup at the tip of the nebulizer. This affects aerosol flow rate causing instrumental drift. Wetting the argon prior to nebulization, the use of a tip washer, or sample dilution have been used to control this problem. Also, it has been reported that better control of the argon flow rate improves instrument performance. This is accomplished with the use of mass flow controllers.

3.1.3 Chemical interferences are characterized by molecular compound formation, ionization effects and solute vaporization effects. Normally these effects are not pronounced with the ICP technique. However, if observed they can be minimized by careful selection of operating conditions (that is, incident power, observation position, and so forth) by buffering of the sample, by matrix matching, and by standard addition procedures. These types of interferences can be highly dependent on matrix type and the specific analyte element.

3.2 For each group of samples of a similar matrix type and concentration (i.e., low, medium) for each Case of samples, or for each 20 samples received, whichever is more frequent, the following tests must be performed prior to reporting concentration data for analyte elements.

3.2.1 Serial dilution - If the analyte concentration is sufficiently high (minimally a factor of 10 above the instrument detection limit after dilution), an analysis of a 1 + 4 dilution must agree within 10 percent of the original determination. Serial dilution results must be reported on the Report Form. Samples identified as field blanks cannot be used for serial dilution analysis.

If the dilution analysis is not within 10 percent, a chemical or physical interference effect should be suspected, and the data must be flagged.

4.0 DEFINITIONS

4.1 Dissolved - Those elements which will pass through a 0.45-um membrane filter.

4.2 Suspended - Those elements which are retained by a 0.45-um membrane filter.

4.3 Total - The concentration determined on an unfiltered sample following vigorous digestion.

4.4 Instrumental detection limits - The instrumental detection limits are determined by multiplying by three the average of the standard deviation obtained from the analysis of a standard solution at a concentration 3 to 5 times the instrument detection limits.

4.5 Sensitivity - The slope of the analytical curve; i.e., functional relationship between emission intensity and concentration.

4.6 Instrument check standard - A multi-element standard of known concentrations prepared by the analyst to monitor and verify instrument performance on a daily basis. (See Section 8.6.1.)

4.7 Interference check sample - A solution containing both interfering and analyte elements of known concentration that can be used to verify background and interelement correction factors. (See Section 8.6.2.)

4.8 Quality control sample - A solution obtained from an outside source having known concentration values to be used to verify the calibration standards. (See Section 8.6.3.)

4.9 Linear dynamic range - The concentration range over which the analytical curve remains linear.

4.10 Reagent blank - A volume of deionized, distilled water contain the same acid matrix as the calibration standards carried through the entire analytical scheme. (See Section 8.5.2.)

4.11 Calibration blank - A volume of deionized, distilled water acidified with nitric acid (HNO_3) and hydrochloric acid (HCl). (See Section 8.5.1.)

4.12 Method of standard addition - The standard addition technique involves the use of the unknown and the unknown-plus-a-known amount of standard by adding known amounts of standard to one or more aliquots of the processed sample solution.

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

5.1 For the determination of trace elements, contamination and loss are prime concerns. Dust in the laboratory environment, impurities in reagents and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. Sample containers can introduce either positive or negative errors in the measurement of trace elements by (a) contributing contaminants through leaching or surface desorption, and (b) by depleting concentrations through adsorption. Thus, the collection and treatment of the sample prior to analysis requires particular attention. Laboratory glassware including the sample bottle (whether polyethylene, polypropylene, or FEP-fluorocarbon) should be thoroughly washed with detergent and tap water, rinsed with HNO_3 (1 + 1), tap water, HCl (1 + 1), tap and finally deionized, distilled water in that order. (See Notes 1 and 2.)

Note 1: Chromic acid may be useful to remove organic deposits from glassware; however, the analyst should be cautioned that the glassware must be thoroughly rinsed with water to remove the last traces of chromium. This is especially important if chromium is to be included in the analytical scheme. A commercial product, NOCHROMIX (available from Godax Laboratories, 6 Varick St., New York, NY, 10013), may be used in place of chromic acid. Chromic acid should not be used with plastic bottles.

Note 2: If it can be documented through an active analytical quality control program using spiked samples and reagent blanks, that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure.

5.2 Sample Preservation

5.2.1 Aqueous samples collected for the determination of total elements are not to be filtered. The sample should be acidified with HNO_3 (1 + 1) to a pH of 2 or less. Normally, 3 mL of HNO_3 (1 + 1) per liter should be sufficient to preserve the sample.

5.2.2 Aqueous samples collected for the determination of dissolved elements must be filtered through a 0.45-um membrane filter as soon as practical after collection. (Glass or plastic filtering apparatus are recommended to avoid possible contamination.) Use the first 50 to 100 mL to rinse the filter flask. Discard this portion and collect the required volume of filtrate. Acidify the filtrate with HNO_3 (1 + 1) to a pH of 2 or less. Normally, 3 mL of HNO_3 (1 + 1) per liter should be sufficient to preserve the sample.

5.2.3 Solid samples collected for the determination of total metals should be mixed thoroughly to achieve homogeneity. Solid samples should be preserved by maintaining them at

4°C for and during shipment to the laboratory. Samples must be refrigerated upon receipt at the laboratory until analysis.

6.0 SAFETY

6.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material handling data sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified (7,8,9) for the information of the analyst.

7.0 APPARATUS AND EQUIPMENT

7.1 Inductively Coupled Plasma-Atomic Emission Spectrometer

7.1.1 Computer controlled atomic emission spectrometer with background correction.

7.1.2 Radiofrequency generator.

7.1.3 Argon gas supply - welding grade or better.

8.0 REAGENTS

8.1 Acids used in the preparation of standards and for sample processing must be ultra-high purity grade or equivalent. Redistilled acids are acceptable.

8.1.1 Acetic acid - Concentrated (sp gr 1.06).

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8.1.2 Hydrochloric acid - Concentrated (sp gr 1.19).

8.1.3 Hydrochloric acid (1 + 1) - Add 500 mL of concentrated HCl (sp gr 1.19) to 400 mL of deionized, distilled water and dilute to 1 L.

8.1.4 Nitric acid - Concentrated (sp gr 1.41).

8.1.5 Nitric acid (1 + 1) - Add 500 mL of concentrated HNO_3 (sp gr 1.41) to 400 mL of deionized, distilled water and dilute to 1 L.

8.2 Deionized, distilled water - Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use deionized, distilled water for the preparation of all reagents, calibration standards and as dilution water. The purity of this water must be equivalent to ASTM Type II reagent water of Specification D 1193(6).

8.3 Standard stock solutions may be purchased or prepared from ultra-high purity grade chemicals or metals. All salts must be dried for 1 h at 105°C unless otherwise specified. Ultra-high purity is defined as 5-9s or better grade chemicals or metals.

(Caution: Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.) Typical stock solution preparation procedures follow.

8.3.1 Aluminum stock solution (1 mL = 100 ug Al) - Dissolve 0.100 g of aluminum metal in an acid mixture of 4 mL of HCl (1 + 1) and 1 mL of concentrated HNO_3 in a beaker. Warm gently to effect solution. When solution is complete, transfer quantitatively to a 1-L flask, add an additional 10 mL of HCl (1 + 1) and dilute to 1000 mL with deionized, distilled water.

8.3.2 Antimony stock solution (1 mL = 100 ug Sb) - Dissolve 0.2669 g of $K(SbO)C_4H_4O_6$ in deionized distilled water, add 10 mL of HCl (1 + 1) and dilute to 1000 mL with deionized, distilled water.

8.3.3 Arsenic stock solution (1 mL = 100 ug As) - Dissolve 0.1320 g of As_2O_3 in 100 mL of deionized, distilled water containing 0.4 g of NaOH. Acidify the solution with 2 mL of concentrated HNO_3 and dilute to 1000 mL with deionized, distilled water.

8.3.4 Barium stock solution (1 mL = 100 ug Ba) - Dissolve 0.1516 g of $BaCl_2$ (dried at 250°C for 2 h) in 10 mL of deionized, distilled water with 1 mL HCl (1 + 1). Add 10.0 mL of HCl (1 + 1) and dilute to 1000 mL with deionized, distilled water.

8.3.5 Beryllium stock solution (1 mL = 100 ug Be) - Do not dry. Dissolve 1.966 g of $BeSO_4 \cdot 4H_2O$ in deionized, distilled water, add 10.0 mL of concentrated HNO_3 and dilute to 1000 mL with deionized, distilled water.

8.3.6 Cadmium stock solution (1 mL = 100 ug Cd) - Dissolve 0.1142 g of CdO in a minimum amount of HNO_3 (1 + 1). Heat to increase rate of dissolution. Add 10.0 mL of concentrated HNO_3 and dilute to 1000 mL with deionized, distilled water.

8.3.7 Calcium stock solution (1 mL = 100 ug Ca) - Suspend 0.2498 g of $CaCO_3$ dried at 180°C for 1 h before weighing in deionized, distilled water and dissolve cautiously with a minimum amount of HNO_3 (1 + 1). Add 10.0 mL of concentrated HNO_3 and dilute to 1000 mL with deionized, distilled water.

8.3.8 Chromium stock solution (1 mL = 100 ug Cr) - Dissolve 0.1923 g of CrO_3 in deionized, distilled water. When solution is complete acidify with 10 mL of concentrated HNO_3 and dilute to 1000 mL with deionized, distilled water.

8.3.9 Cobalt stock solution (1 mL = 100 ug Co) - Dissolve 0.1000 g of cobalt metal in a minimum amount of HNO_3 (1 + 1). Add 10.0 mL of HCl (1 + 1) and dilute to 1000 mL with deionized, distilled water.

8.3.10 Copper stock solution (1 mL = 100 ug Cu) - Dissolve 0.1252 g of CuO in a minimum amount of HNO_3 (1 + 1). Add 10.0 mL of concentrated HNO_3 and dilute to 1000 mL with deionized, distilled water.

8.3.11 Iron stock solution (1 mL = 100 ug Fe) - Dissolve 0.1430 g of Fe_2O_3 in a warm mixture of 20 mL of HCl (1 + 1) and 2 mL of concentrated HNO_3. Cool, add an additional 5 mL of concentrated HNO_3 and dilute to 1000 mL with deionized, distilled water.

8.3.12 Lead stock solution (1 mL = 100 ug Pb) - Dissolve 0.1599 g of $Pb(NO_3)_2$ in a minimum amount of HNO_3 (1 + 1). Add 10.0 mL of concentrated HNO_3 and dilute to 1000 mL with deionized, distilled water.

8.3.13 Magnesium stock solution (1 mL = 100 ug Mg) - Dissolve 0.1658 g of MgO in a minimum amount of HNO_3 (1 + 1). Add 10.0 mL of concentrated HNO_3 and dilute to 1000 mL with deionized, distilled water.

8.3.14 Manganese stock solution (1 mL = 100 ug Mn) - Dissolve 0.1000 g of manganese metal in the acid mixture, 10 mL of concentrated HCl and 1 mL of concentrated HNO_3, and dilute to 1000 mL with deionized, distilled water.

8.3.15 Molybdenum stock solution (1 mL = 100 ug Mo) - Dissolve 0.2043 g of $(NH_4)_2MoO_4$ in deionized, distilled water and dilute to 1000 mL.

8.3.16 Nickel stock solution (1 mL = 100 ug Ni) - Dissolve 0.1000 g of nickel metal in 10 mL of hot concentrated HNO_3, cool and dilute to 1000 mL with deionized, distilled water.

8.3.17 Potassium stock solution (1 mL = 100 ug K) - Dissolve 0.1907 g of KCl, dried at 110°C, in deionized, distilled water. Dilute to 1000 mL.

8.3.18 Selenium stock solution (1 mL = 100 ug Se) - Do not dry. Dissolve 0.1727 g of H_2SeO_3 in deionized, distilled water and dilute to 1000 mL.

8.3.19 Silver stock solution (1 mL = 100 ug Ag) - Dissolve 0.1575 g of $AgNO_3$ in 100 mL of deionized, distilled water and 10 mL concentrated HNO_3. Dilute to 1000 mL with deionized, distilled water.

8.3.20 Sodium stock solution (1 mL = 100 ug Na) - Dissolve 0.2542 g of NaCl in deionized, distilled water. Add 10.0 mL of concentrated HNO_3 and dilute to 1000 mL with deionized, distilled water.

8.3.21 Thallium stock solution (1 mL = 100 ug Tl) - Dissolve 0.1303 g of $TlNO_3$ in deionized, distilled water. Add 10.0 mL of concetrated HNO_3 and dilute to 1000 mL with deionized, distilled water.

8.3.22 Vanadium stock solution (1 mL = 100 ug V) - Dissolve 0.2297 g of NH_4VO_3 in a minimum amount of concentrated HNO_3. Heat to increase rate of dissolution. Add 10.0 mL of concentrated HNO_3 and dilute to 1000 mL with deionized, distilled water.

8.3.23 Zinc stock solution (1 mL = 100 ug Zn) - Dissolve 0.1245 g of ZnO in a minimum amount of dilute HNO_3. Add 10.0 mL of concentrated HNO_3 and dilute to 1000 mL with deionized, distilled water.

8.4 Mixed calibration standard solutions - Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks. (See Sections 8.4.1 through 8.4.5.) Add 2 mL of HNO_3 (1 + 1) and 10 mL of HCl (1 + 1) and dilute to 100 mL with deionized, distilled water. (See Note 3.) Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standard solutions to a FEP fluorocarbon or unused polyethylene bottle for storage. Fresh mixed standards should be prepared as needed with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample and monitored weekly for stability (see Section 8.6.3). Although not specifically required, some typical calibration standard combinations follow when using the specific wavelengths listed in Table 1.

8.4.1 Mixed standard solution I - Manganese, beryllium, cadmium, lead, and zinc.

8.4.2 Mixed standard solution II - Barium, copper, iron, vanadium, and cobalt.

8.4.3 Mixed standard solution III - Molybdenum, arsenic, and selenium.

8.4.4 Mixed standard solution IV - Calcium, sodium, potassium, aluminum, chromium, and nickel.

8.4.5 Mixed standard solution V - Antimony, magnesium, silver, and thallium.

Note 3: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of deionized, distilled water and warm the flask until the solution clears. Cool and dilute to 100 mL with deionized, distilled water. For this acid combination the silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap water matrix for 30 d. Higher concentrations of silver require additional HCl.

8.5 Two types of blanks are required for the analysis. The calibration blank (Section 4.11) is used in establishing the analytical curve while the reagent blank (Section 4.10) is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

8.5.1 The calibration blank is prepared by diluting 2 mL of HNO_3 (1 + 1) and 10 mL of HCl (1 + 1) to 100 mL with deionized, distilled water. Prepare a sufficient quantity to be used to flush the system between standards and samples.

8.5.2 The reagent blank must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentrations in the final solution as the sample solution used for analysis.

8.6 In addition to the calibration standards, an instrument check standard (Section 4.6), an interference check sample (Section 4.7), and a quality control sample (Section 4.8) are also required for analyses.

8.6.1 The instrument check standard for continuing calibration verification is prepared by the analyst by combining compatible elements at a concentration equivalent to the mid-point of their respective calibration curves. (See Section 13.1.3.)

8.6.2 The interference check sample is prepared by the analyst, or obtained from EPA if available.

8.6.3 The quality control sample for the initial calibration verification should be prepared in the same acid matrix as the calibration standards and in accordance with the instructions provided by the supplier. EPA will either supply a quality control sample or information where one of equal quality can be procured. (See Section 13.1.1.)

9.0 CALIBRATION

9.1 Calibration Standards - Because of the differences in the response of the various instrument configurations and in the selection of analytical wavelengths, no specific concentration can be provided. Instead, the analyst should establish the appropriate calibration standard concentration for each individual analyte line on that particular instrument. Some typical calibration standard combinations are reported in Section 8.4.

9.2 Instrument Operating Conditions - Because of the differences between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of the particular instrument. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be investigated and established for each individual analyte line on that particular instrument. All measurements must be within the instrument linear range where correction factors are valid. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions used satisfy the analytical requirements and to maintain quality control data confirming instrument performance and analytical results. General instrument calibration should include:

9.2.1 Set up instrument with proper operating parameters established in Section 9.2. The instrument must be allowed to become thermally stable before beginning. This usually requires at least 30 min of operation prior to calibration.

9.2.2 Initiate appropriate operating configuration of computer.

9.2.3 Profile and calibrate instrument according to instrument manufacturer's recommended procedures, using mixed calibration standard solutions such as those described in Section 8.4. Flush the system with the calibration blank (Section 8.5.1) between each standard. (Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.)

9.2.4 Begin the sample run flushing the system with the calibration blank (Section 8.5.1) between each sample. Analyze the instrument check standard (Section 8.6.1) and the calibration blank (Section 8.5.1) each 10 samples.

10.0 PROCEDURE

10.1 Aqueous Samples

For the determination of elements in aqueous samples, shake sample and transfer 100 mL of a well-mixed sample to a 250-mL beaker. Add 2 mL of HNO_3 (1 + 1) and 10 mL of HCl (1 + 1) to the sample. Cover with watch glass or similar cover and heat on a steam bath or hot plate until the volume has been reduced to between 25 and 50 mL making certain the sample does not boil.

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After this treatment, cool sample and filter to remove insoluble material that could clog the nebulizer. (See Note 4.) Adjust the volume to 100 mL with deionized distilled water. The sample is now ready for analysis.

Concentrations so determined shall be reported as "total."

Note 4: In place of filtering, the sample after dilution and mixing may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

10.2 Solid Samples

10.2.1 For the determination of elements in solid samples, e.g., sediments, sludges, and soils, mix the sample thoroughly to achieve homogeneity. For each digestion procedure, weigh (to the nearest 0.01 g) a 1.0 to 1.5-g portion of sample and transfer to a 100-mL beaker.

10.2.2 Add 10 mL of HNO_3 (1 + 1), mix the slurry, and cover with a watch glass. Heat the sample to 95°C and reflux for 10 min without boiling. Allow the sample to cool, add 5 mL of concentrated HNO_3, replace the watch glass, and reflux for 30 min. Do not allow the volume to be reduced to less than 5 mL while maintaining a covering of solution over the bottom of the beaker.

10.2.3 After the second reflux step has been completed and the sample has cooled, add 2 mL of Type II water and 3 mL of 30 percent hydrogen peroxide (H_2O_2). Return the beaker to the hot plate for warming to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides, and cool the beaker.

Continue to add 30 percent H_2O_2 in 1-mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged. (NOTE: Do not add more than a total of 10 mL of 30 percent H_2O_2.)

10.2.4 Next, add 5 mL of HCl (1 + 1) and 10 mL of Type II water, return the covered beaker to the hot plate, and heat for an additional 10 min. After cooling, filter through Whatman No. 42 filter paper (or equivalent, or centrifuge the sample - see Note 4). Dilute the digestate to 200 mL (final volume) with deionized, distilled water. The sample is now ready for analysis.

11.0 CALCULATIONS

11.1 Reagent blanks should be analyzed for each Case and used in all analyses to ascertain whether sample concentrations reflect contamination in the following manner:

11.1.1 If the concentration of the blank is less than or equal to the CRDL or MDL, no correction of sample results is performed.

11.1.2 If the concentration of the blank is above the CRDL or MDL for any group of samples associated with a particular blank, the concentration of the sample with the least concentrated analyte must be 10 times the blank concentration, or all samples associated with the blank and less than 10 times the blank concentration must be redigested and re-analyzed, with the exception of an identified aqueous soil field blank value. The fact that a blank concentration was observed should be documented in the Case Narrative. The sample value is not to be corrected for the blank value.

11.2 If dilutions were performed, the appropriate factor must be applied to sample values.

11.3 Units must be clearly specified.

11.4 A separate determination of percent solids must be performed (Figure 1).

11.4.1 The concentrations determined in the digest for solid samples are to be reported on the basis of the dry weight of the sample.

$$\text{Concentration (dry wt.) (mg/kg)} = \frac{C \times V}{W \times S}$$

where:

C = Concentration (mg/L)

V = Final volume after sample preparation (L)

W = Weight of wet sample (kg)

S = % Solids/100.

12.0 REPORTING

12.1 All reports in the sample data package must be submitted in a legible form.

12.1.1 The data report package for analyses of each sample must be complete before submission and shall include:

12.1.1.1 The cover page for the Survey Inorganic Analysis data package (see Figure 2) including DOE/ES and laboratory cross reference numbers, Case Narrative (comments), footnotes used in the data package, and the statement on the use of ICP background and interelement corrections for the samples. The type of inorganic analyses data package including CLP Inorganic Analyses Data Package or a combination of the following ICP Inorganic Analyses Data Package, Furnace AA Inorganic Analysis Data Package, and/or Cold Vapor AA Analyses Data Package.

12.1.1.2 Tabulated results in ug/L for aqueous samples or mg/kg for solid samples (identification and quantity) of specified chemical constituents (Table 1) by the specified analyses validated and signed in original signature by the Laboratory Manager, and reported on Form I (Figure 3). The results for solid samples will be reported on a dry-weight basis. Percent solids are not required on aqueous samples. If the value or the result is greater than or equal to the Instrument Detection Limit (IDL), corrected for dilutions, report the value. All dilutions not required by the contract and affecting the IDL, must be noted on an element by element basis on Form I. If results are being reported for the CLP Inorganic Analyses Data Package, the following instruction for reporting the value should be followed. If the value is less than the CRDL in Table 1, put the value in brackets (e.g., [10]). If the element was analyzed for but not detected, report the instrument detection limit value with a "U" (e.g., 10U). If results are being reported for the ICP Inorganic Analyses Data Package, use the same basic format except use the ICP Method Detection Levels instead of the CLP CRDL. The following are common in both data reporting packages: use an "E" as the footnote to indicate an estimate value or value not reported due to the presence of interference as observed in the serial dilution sample. If the duplicate sample analysis is not within the control limits, flag it with an asterisk (*). If the spike sample recovery is not within control limits, flag the data with the letter N. Note any sample problems in the Case Narrative. Report results to two significant figures for values from 0 to 100 and three significant figures for results greater than 100. For rounding rules, follow the EPA Handbook of Analytical Quality Control in Water and Wastewater Laboratories(3).

12.1.1.3 The spike sample recovery should be reported on Form V (Spike Sample Recovery, Figure 4) and included in the data package.

12.1.1.4 The duplicate sample analysis results should be reported on Form VI (Duplicates, Figure 5) and included in the data package.

12.1.1.5 The ICP serial dilution sample results should be reported on Form IX (ICP Serial Dilution, Figure 6) and included in the data package.

12.1.1.6 For the CLP Inorganic Analyses Data Package, sample results should be reported on Forms II, III, IV, VII, XI, XII, and XIII (Figures 7, 8, 9, 10, 11 and 12, 13 and 14, and 15, respectively). These forms are not required for results being reported using the DOE Environmental Survey ICP Method.

13.0 QUALITY ASSURANCE/QUALITY CONTROL

13.1 Check the instrument standardization by analyzing appropriate quality control check standards as follows.

13.1.1 A quality control sample (Section 8.6.3) must be used daily for the initial calibration verification. A fresh dilution of this sample shall be analyzed every week thereafter to monitor their stability. If the Initial Calibration Verification Solutions(s) are not available from EPA, or where a certified solution of an analyte is not available from any source, analyses shall be conducted on an independent standard at a concentration other than that used for calibration, but within the calibration range. An independent standard is defined as a standard composed of the analytes from a source different than those used in the standards for the initial calibration. For ICP, the Initial Calibration Verification Solution(s) must be run at each wavelength used in the analysis of the sample. When measurements exceed the control limits of ±10 percent, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified.

13.1.2 Analyze the calibration blank (Section 8.5.1) at a frequency of 10 percent. Blanks are to be reported down to the IDL. If the blank result is greater than the MDL or CRDL, terminate the analysis, correct the problem and recalibrate the instrument.

13.1.3 For continuing calibration verification, analyze an appropriate instrument check standard (Section 8.6.1) containing the elements of interest at a frequency of 10 percent. This check standard is used to determine instrument drift. If agreement is not within ±10 percent of the expected values, the analysis is out of control. The analysis must be terminated, the problem corrected, the instrument recalibrated, and the preceding 10 samples re-analyzed.

13.1.4 To verify interelement and background correction factors, analyze the ICP interference check sample (Section 8.6.2) at the beginning and end of the sample run or a minimum of twice per 8-h work shift, whichever is more frequent. The ICP Interference Check Sample must be obtained from EPA's Environmental Monitoring Service Laboratory - Las Vegas, Nevada (EMSL-LV) if available. Results for the check sample analysis during the analytical runs must fall within the control limit of ±20 percent of the true value for the analytes included in the Interference Check Sample. If not, terminate the analysis, correct the problem, recalibrate, reverify the calibration, and re-analyze the samples. If the ICP Interference Check Sample is not available from EPA, an independent ICP Check Sample must be prepared with interferent and analyte concentrations at the levels specified in Table 5. The mean value and standard deviation of an independent ICP Interference Check Standard must be established by initially analyzing the check samples at least 5 times repetitively for each parameter. Results must fall within the control limit of ±20 percent of the established mean value.

13.1.5 To check for physical and/or chemical interference effects, analyze for each group of samples of a similar matrix type and concentration (i.e., low, medium) for each Case of samples, or for each 20 samples received, whichever is more frequent, a 1 + 4 serial dilution prior to reporting concentration data for the analyte elements. If the analyte concentration is sufficiently high (minimally a factor of 10 above the instrument detection limit after dilution), an analysis of a 1 + 4 dilution must agree within 10 percent of the original determination. Samples identified as field blanks cannot be used for serial dilution analysis.

If the dilution analysis is not within 10 percent, a chemical or physical interference effect should be suspected, and the data must be flagged with an "E." This observation should be documented in the Case Narrative and reported on Form I (Figure 3).

13.1.6 The spiked sample analysis is designed to provide information about the effect of the sample matrix on the digestion and measurement methodology. The spike is added before the digestion steps. At least one spiked sample analysis must be performed on each group of samples of a similar matrix type (i.e., water, soil) and concentration (i.e., low, medium) for each Case of samples or for each 20 samples received, whichever is more frequent. Samples identified as field blanks cannot be used for spiked sample analysis. The analyte spike must be added in the amount given in Table 6 for each element analyzed. If the spike recovery is not within the limits of 75 to 125 percent, the data of all samples received associated with that spiked sample must be flagged with the letter "N" on Forms I and IX (Figures 3 and 6). An exception to this rule is granted in situations where the sample concentration exceeds the spike concentration by a factor of four or more. In such a case, the spike recovery should not be considered and the data shall be reported unflagged even if the percent recovery does not meet the 75-to 125-percent recovery criteria. In the instance where there is more than one spiked sample per matrix per Case, if one spike sample recovery is not within contract criteria, flag all the samples of the same matrix in the Case. Individual component percent recoveries are calculated as follows using the following equation.

$$\text{Percent Recovery} = \frac{(SSR-SR)}{SA} \times 100$$

where:

SSR = Spiked sample result

SR = Sample result

SA = Spike added.

13.1.7 At least one duplicate sample must be analyzed from each group of samples of a similar matrix type (i.e., water, soil) and concentration (i.e., low, medium) for each Case of samples or for each 20 samples received, whichever is more frequent. Samples identified as field blanks cannot be used for duplicate sample analysis. The relative percent differences (RPD) for each component are calculated using the following equation.

$$RPD = \frac{|D_1 - D_2|}{(D_1 + D_2)/2} \times 100$$

where:

D_1 = First sample value

D_2 = Second sample value (duplicate).

The results of the duplicate sample analysis must be reported on Form VI (Figure 5). A control limit of ±20 percent for RPD shall be used for sample values greater than 5 times the CRDL for the CLP Data Package or method detection level (MDL) for the ICP Method. A control limit of + the CRDL or MDL shall be used for sample values less than 5 times the CRDL or MDL (Table 1), and this control limit (±CRDL or ±MDL) should be entered in the "Control Limit" column on Form VI (Figure 5). If one result is above the 5 x CRDL or MDL level and the other is below, use the ±MDL criterion. If either sample value is less than the CRDL or MDL, the RPD is not calculated and is indicated as "NC" on Form VI.

If the duplicate sample results are outside the control limits, flag all the data for samples received associated with that duplicate sample with an "*" on Forms I and VI (Figures 3 and 5). In the instance where there is more than one duplicate sample per Case, if one duplicate result is not within contract criteria, flag all the samples of the same matrix in the Case.

14.0 REFERENCES

1. Winge, R. K., V. J. Peterson, and V. A. Fassel. "Inductively Coupled Plasma-Atomic Emission Spectroscopy Prominent Lines," EPA-600/4-79-017.

2. Winefordner, J. D. "Trace Analysis: Spectroscopic Methods for Elements," Chemical Analysis, 46, pp. 41-42.

3. EPA (U.S. Environmental Protection Agency). Handbook for Analytical Quality Control in Water and Wastewater Laboratories, EPA-600/4-79-019, Cincinnati, Ohio.

4. Garbarino, J. R., and H. E. Taylor, 1979. "An Inductively Coupled Plasma Emission Spectrometric Method for Routine Quality Testing," Applied Spectroscopy 33, No. 3.

5. EPA (U.S. Environmental Protection Agency). "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020.

6. Annual Book of ASTM Standards, Part 31.

7. Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, 1977. "Carcinogens - Working with Carcinogens," Publication No. 77-206.

8. Occupational Safety and Health Administration, January 1976. "OSHA Safety and Health Standards, General Industry" (29 CFR 1910), OSHA 2206.

9. Committee on Chemical Safety, 1979. "Safety in Academic Laboratories," American Society Publications, 3rd Edition.

10. Martin, T. D. (EMSL/Cincinnati). "Inductively Coupled Plasma-Atomic Emission Spectrometric Method of Trace Element Analysis of Water and Waste," Method 200.7 modified by CLP Inorganic Data/Protocol Review Committee.

11. Lindahl, P. C. (Argonne National Laboratory). "Inductively Coupled Plasma-Atomic Emission Spectrometric Method for Trace Element Analysis of Aqueous and Solid Samples," modified from the Contract Laboratory Program, SOW No. 785.

Table 1. Elements Determined by ICP Analysis Method

Element	ICP Method Detection Levels[a] (ug/L)	CLP Contract Required Detection Levels[b] (ug/L)
Aluminum	200	200
Antimony	150	60[c]
Arsenic	250	10[c]
Barium	200	200
Beryllium	5	5
Cadmium	20	5[c]
Calcium	5000	5000
Chromium	10	10
Cobalt	50	50
Copper	25	25
Iron	100	5[c]
Lead	200	200
Magnesium	5000	5000
Manganese	15	15
Mercury	ND[d]	0.2
Nickel	40	40
Potassium	5000	5000
Selenium	400	5[c]
Silver	30	10[c]
Sodium	5000	5000
Thallium	100	10[c]
Vanadium	50	50
Zinc	20	20

a. These MDL are the instrument detection limits obtained in pure water that must be met using the procedure. The detection limits for samples may be considerably higher depending on the sample matrix.

b. These CRDL are the ICP, Furnace AA, and Cold Vapor AA detection limits obtained in pure water that must be met using the procedure. The detection limits for samples may be considerably higher depending on the sample matrix.

c. Furnace AA is usually required to attain the CRDLs for these elements.

d. ND is not determined. Mercury is not determined in the ICP method.

Table 2. Recommended Wavelengths and Estimated Instrumental Detection Limits

Element	Wavelength (nm)[a]	Estimated Instrumental Detection Limit (ug/L)[b]
Aluminum	308.215	45
Antimony	206.833	32
Arsenic	193.696	53
Barium	455.403	2
Beryllium	313.042	0.3
Cadmium	226.502	4
Calcium	317.933	10
Chromium	267.716	7
Cobalt	228.616	7
Copper	324.754	6
Iron	259.940	7
Lead	220.353	42
Magnesium	279.079	30
Manganese	257.610	2
[illegible]kel	231.604	15
Potassium	766.491	--[c]
Selenium	196.026	75
Silver	328.068	7
Sodium	588.995	29
Thallium	190.864	40
Vanadium	292.402	8
Zinc	213.856	2

a. The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelength may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference. (See Section 5.1.1). The use of alternate wavelengths must be reported (in nm) with the sample data.

b. The estimated instrumental detection limits, as shown, are taken from "Inductively Coupled Plasma-Atomic Emission Spectroscopy-Prominent Lines," EPA-600-4-79-017. They are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

c. Highly dependent on operating conditions and plasma position.

Table 3. Example of Analyte Concentration Equivalents (mg/L) Arising from Interferents at the 100 mg/L Level

Analyte	Wavelength (nm)	Interferent									
		Al	Ce	Cr	Cu	Fe	Mg	Mn	Ni	Ti	V
Aluminum	308.215	--	--	--	--	--	--	0.21	--	--	1.4
Antimony	206.833	0.47	--	2.9	--	0.08	--	--	--	.25	0.45
Arsenic	193.696	1.3	--	0.44	--	--	--	--	--	--	1.1
Barium	455.403	--	--	--	--	--	--	--	--	--	--
Beryllium	313.042	--	--	--	--	--	--	--	--	0.04	0.05
Boron	249.773	0.04	--	--	--	0.32	--	--	--	--	--
Cadmium	226.502	--	--	--	--	0.03	--	--	0.02	--	--
Calcium	317.933	--	--	0.08	--	0.01	0.01	0.04	--	0.03	0.03
Chromium	267.716	--	--	--	--	0.003	--	0.04	--	--	0.04
Cobalt	228.616	--	--	0.03	--	0.005	--	--	0.03	0.15	--
Copper	324.754	--	--	--	--	0.003	--	--	--	0.05	0.02
Iron	259.940	--	--	--	--	--	--	0.12	--	--	--
Lead	220.353	0.17	--	--	--	--	--	--	--	--	--
Magnesium	279.079	--	0.02	0.11	--	0.13	--	0.25	--	0.07	0.12
Manganese	257.610	0.005	--	0.01	--	0.002	0.002	--	--	--	--
Molybdenum	202.030	0.05	--	--	--	0.03	--	--	--	--	--
Nickel	231.604	--	--	--	--	--	--	--	--	--	--
Selenium	196.026	0.23	--	--	--	0.09	--	--	--	--	--
Silicon	288.158	--	--	0.07	--	--	--	--	--	--	0.01
Sodium	588.995	--	--	--	--	--	--	--	--	0.08	--
Thallium	190.864	0.30	--	--	--	--	--	--	--	--	--
Vanadium	292.402	--	--	0.05	--	0.005	--	--	--	0.02	--
Zinc	213.856	--	--	--	0.14	--	--	--	0.29	--	--

Table 4. Interferent and Analyte Elemental Concentrations Used for Interference Measurements in Table 3

Analytes	(mg/L)	Interferents	(mg/L)
Al	10	Al	1,000
As	10	Ca	1,000
B	10	Cr	200
Ba	1	Cu	200
Be	1	Fe	1,000
Ca	1	Mg	1,000
Cd	10	Mn	200
Co	1	Ni	200
Cr	1	Ti	200
Cu	1	V	200
Fe	1		
Mg	1		
Mn	1		
Mo	10		
Na	10		
Ni	10		
Pb	10		
Sb	10		
Se	10		
Si	1		
Ti	10		
V	1		
Zn	10		

Table 5. Interferent and Analyte Elemental Concentrations Used for ICP Interference Check Sample

Analytes	(mg/L)	Interferents	(mg/L)
Ba	0.5	Al	500
Be	0.5	Ca	500
Cd	1.0	Fe	200
Co	0.5	Mg	500
Cr	0.5		
Cu	0.5		
Mn	0.5		
Ni	1.0		
Pb	1.0		
V	0.5		
Zn	1.0		

Table 6. Spiking Levels for Spiked Sample Analysis[a,b]

Element	Water (ug/L)	Sediment (ug/L)
Aluminum	2,000	NR
Antimony	500	500
Arsenic	2,000	2,000
Barium	2,000	2,000
Beryllium	50	50
Cadmium	50	50
Calcium	NR	NR
Chromium	200	200
Cobalt	500	500
Copper	250	250
Iron	1,000	NR
Lead	500	500
Magnesium	NR	NR
Manganese	200	500
Nickel	400	500
Potassium	NR	NR
Selenium	2,000	2,000
Silver	50	50
Sodium	NR	NR
Thallium	2,000	2,000
Vanadium	500	500
Zinc	200	500

a. The levels shown indicate concentrations in the final digestate of the spiked sample (200 mL final volume).

b. NR = No spike required.

1. Add a portion of the sample to a tared weighing dish. Weigh and record the weight.

2. Place weighing dish plus sample, with the cover tipped to allow for moisture escape, in a drying oven that is set at 103° to 105°C. Perform this task in a well-ventilated area.

3. Dry the sample to constant weight. Cool the sample in a desiccator with the weighing dish cover in place before each weighing. Record each weight. Do not analyze the dried sample.

4. Calculate and report data on a dry weight basis. Also report the percent solids for each sample.

$$\text{Percent solids} = \frac{\text{Sample Dry Weight}}{\text{Sample Wet Weight}} \times 100$$

Figure 1. Determination of Percent Solids

Date ____________

COVER PAGE
ICP ANALYSES DATA PACKAGE

Lab Name ____________________
____

Case No. ____________________
Q.C. Report No.

Sample Numbers

DOE No.	Lab ID No.	DOE No.	Lab ID No.

Comments:____

Inorganic Analyses Data Package for USEPA CLP Method ________
if not indicate the method or method combinations
DOE ES ICP Method ________
DOE ES Furnace AA Method ________
DOE ES Cold Vapor AA Method ________
ICP interelement and background corrections applied? Yes ___ No ___.
If yes, corrections applied before ___ or after ___ generation of raw data.

Footnotes:

NR	- Not required at this time.
Form I:	
Value	- If the result is a value greater than or equal to the instrument detection limit but less than the required detection limit (See DOE methods), report the value in brackets (i.e., [10]).
U	- Indicates element was analyzed for but not detected. Report with the instrument detection limit value (e.g., [10U]).
E	- Indicates a value estimated or not reported due to the presence of interference. Explanatory note included on cover page.
S	- Indicates value determined by Method of Standard Additions.
N	- Indicates spike sample recovery is not within control limits.
*	- Indicates duplicate analysis is not within control limits.
+	- Indicates the correlation coefficient for method of standard additions is less than 0.995.
M	- Indicates duplicate injection results exceed control limits.

Indicate method used: P for ICP; A for Flame AA; F for Furnace AA; and C for Cold Vapor AA.

Figure 2. Cover Page, ICP Analyses Data Package

9212[illegible]570978

Form I

Date ______

INORGANIC ANALYSIS DATA SHEET

Lab Name ______________

____

Case No. ______________

Lab Receipt Date ______

Lab Sample ID. No. ______

QC Report No. ______________

Elements Identified and Measured

Concentration: Low ______ Medium ______

Matrix: Water ____ Soil ______ Sludge ______ Other ______

ug/L or mg/kg dry weight (Circle One)

1. Aluminum ______________
2. Antimony ______________
3. Arsenic ______________
4. Barium ______________
5. Beryllium ______________
6. Cadmium ______________
7. Calcium ______________
8. Chromium ______________
9. Cobalt ______________
10. Copper ______________
11. Iron ______________
12. Lead ______________
13. Magnesium ______________
14. Manganese ______________
15. Mercury ______________
16. Nickel ______________
17. Potassium ______________
18. Selenium ______________
19. Silver ______________
20. Sodium ______________
21. Thallium ______________
22. Vanadium ______________
23. Zinc ______________

Percent Solids (%) ______________

Footnotes: For reporting results to EPA, standard result qualifiers are used as defined on Cover Page. Additional flags or footnotes explaining results are encouraged. Definition of such flags must be explicit and contained on Cover Page, however.

Comments: ______________________________

____

____

____

Lab Manager ______________

Figure 3. Inorganic Analysis Data Sheet

Form V

Q.C. Report No. ____________

SPIKE SAMPLE RECOVERY

Lab Name ____________________

Date ____________________

Case No. ____________________

DOE Sample No. ____________

Lab Sample ID No. ________

Units ____________________

Matrix ____________________

Compound	Control Limit %R	Spiked Sample Result (SSR)	Sample Result (SR)	Spiked Added (SA)	[1] %R
Metals:					
1. Aluminum	75-125				
2. Antimony	"				
3. Arsenic	"				
4. Barium	"				
5. Beryllium	"				
6. Cadmium	"				
7. Calcium	"				
8. Chromium	"				
9. Cobalt	"				
10. Copper	"				
11. Iron	"				
12. Lead	"				
13. Magnesium	"				
14. Manganese	"				
15. Mercury	"				
16. Nickel	"				
17. Potassium	"				
18. Selenium	"				
19. Silver	"				
20. Sodium	"				
21. Thallium	"				
22. Vanadium	"				
23. Zinc					
Other:					
Cyanide					

[1] %R = [(SSR - SR)/SA] x 100

"N" - Out of control

"NR" - Not required

Comments: ____

____

Figure 4. Spike Sample Recovery

Form VI
Q.C. Report No. __________
DUPLICATES

LAB NAME ____________________

DATE ________________________

CASE NO. ______________
DOE Sample No. ________
Lab Sample ID No. ______
Units _______________

Matrix ______________

Compound	Control Limit[1]	Sample (S)	Duplicate(D)	RPD[2]
Metals:				
1. Aluminum				
2. Antimony				
3. Arsenic				
4. Barium				
5. Beryllium				
6. Cadmium				
7. Calcium				
8. Chromium				
9. Cobalt				
10. Copper				
11. Iron				
12. Lead				
13. Magnesium				
14. Manganese				
15. Mercury				
16. Nickel				
17. Potassium				
18. Selenium				
19. Silver				
20. Sodium				
21. Thallium				
22. Vanadium				
23. Zinc				
Other ______				
Cyanide				

* Out of Control

[1] To be added at a later date.

[2] $\text{RPD} = \frac{|S - D|}{(S + D)/2} \times 100$

NC - Non calculable RPD due to value(s) less than CRDL

Figure 5. Duplicates

Form IX
Q.C. Report No. ____________
ICP SERIAL DILUTIONS

LAB NAME ____________________
DATE ____________________

CASE NO. ____________________
DOE SAMPLE NO. ______________
LAB SAMPLE ID NO. ___________
Units: ug/L

Matrix ____________________

Compound	Initial Sample Concentration(1)	Serial Dilution[1] Result(s)	% Difference[2]
Metals:			
1. Aluminum			
2. Antimony			
3. Arsenic			
4. Barium			
5. Beryllium			
6. Cadmium			
7. Calcium			
8. Chromium			
9. Cobalt			
10. Copper			
11. Iron			
12. Lead			
13. Magnesium			
14. Manganese			
15. Nickel			
16. Potassium			
17. Selenium			
18. Silver			
19. Sodium			
20. Thallium			
21. Vanadium			
22. Zinc			
Other: ____			

[1] Diluted sample concentration corrected for (1 + 4) dilution

[2] Percent Difference = $\frac{[I - S]}{I} \times 100$

NR - Not Required, initial sample concentration less than 10 times IDL.

Figure 6. ICP Serial Dilutions

Form II

Q.C. Report No. ____________

INITIAL AND CONTINUING CALIBRATION VERIFICATION[3]

LAB NAME ________________________

CASE NO. ________________________

SOW NO. ________________________

DATE ________________________

UNITS ________________________

Compound	Initial[1]Calib.			Continuing Calibration[2]					
Metals:	True Value	Found	%R	True Value	Found	%R	Found	%R	Method
1. Aluminum									
2. Antimony									
3. Arsenic									
4. Barium									
5. Beryllium									
6. Cadmium									
7. Calcium									
8. Chromium									
9. Cobalt									
10. Copper									
11. Iron									
12. Lead									
13. Magnesium									
14. Manganese									
15. Mercury									
16. Nickel									
17. Potassium									
18. Selenium									
19. Silver									
20. Sodium									
21. Thallium									
22. Vanadium									
23. Zinc									

Other: ____

Cyanide ____

[1] Initial Calibration Source________ Continuing Calibration Source_______

[2] Control Limits: Mercury and Tin 80-120; All Other Compounds 90-110

Indicate Analytical Method Used: P - ICP/Flame AA; F - Furnace

Figure 7. Initial and Continuing Calibration Verification

Form III
Q.C. Report No. ________
BLANKS

LAB NAME ____________________ CASE NO. ____________________
DATE ____________________ UNITS ____________________

Compound	Initial Calibration Blank Value	Continuing Calibration Blank Value				Preparation Blank	
		1	2	3	4	1	2
Metals:							
1. Aluminum							
2. Antimony							
3. Arsenic							
4. Barium							
5. Beryllium							
6. Cadmium							
7. Calcium							
8. Chromium							
9. Cobalt							
10. Copper							
11. Iron							
12. Lead							
13. Magnesium							
14. Manganese							
15. Mercury							
16. Nickel							
17. Potassium							
18. Selenium							
19. Silver							
20. Sodium							
21. Thallium							
22. Vanadium							
23. Zinc							
Other: ________							
Cyanide							

Figure 8. Blanks

Form IV
Q.C. Report No. ____________
ICP INTERFERENCE CHECK SAMPLE

LAB NAME ____________________
DATE ____________________

CASE NO. ____________________
Check Sample I.D. ____________
Check Sample Source ____________
Units ____________________

Compound	Control Limits[1]		True[2]	Initial		Final	
	Mean	Std. Dev.		Observed	%R	Observed	%R
Metals:							
1. Aluminum							
2. Antimony							
3. Arsenic							
4. Barium							
5. Beryllium							
6. Cadmium							
7. Calcium							
8. Chromium							
9. Cobalt							
10. Copper							
11. Iron							
12. Lead							
13. Magnesium							
14. Manganese							
15. Mercury							
16. Nickel							
17. Potassium							
18. Selenium							
19. Silver							
20. Sodium							
21. Thallium							
22. Vanadium							
23. Zinc							
Other:							

[1] Mean value based on n = ________.

[2] True Value of EPA ICP Interference Check Sample or contractor standard.

Figure 9. ICP Interference Check Sample

Form VII

Q.C. Report No. ____________

INSTRUMENT DETECTION LIMITS AND LABORATORY CONTROL SAMPLE

LAB NAME ____________________ CASE NO. ______________________

DATE ____________________ LCS NO. ______________________

Compound	Required Detection Limits (CRDL)-ug/L	Instrument Detection Limits (IDL)-ug/L ICP/AA	Furnace	Lab Control Sample ug/L mg/kg (Circle One) True	Found	%R
		ID NO. __	ID NO. __			
Metals:						
1. Aluminum	200					
2. Antimony	60					
3. Arsenic	10					
4. Barium	200					
5. Beryllium	5					
6. Cadmium	5					
7. Calcium	5000					
8. Chromium	10					
9. Cobalt	50					
10. Copper	25					
11. Iron	100					
12. Lead	5					
13. Magnesium	5000					
14. Manganese	15					
15. Mercury	0.2					
16. Nickel	40					
17. Potassium	5000					
18. Selenium	5					
19. Silver	10					
20. Sodium	5000					
21. Thallium	10					
22. Vanadium	50					
23. Zinc	20					
Other: ______						
Cyanide	10					

Figure 10. Instrument Detection Limits and Laboratory Control Sample

Form XIa (Quarterly)
INSTRUMENT DETECTION LIMITS - ICP/AA

LAB NAME ____________________ DATE ____________________

ICP/Flame AA (Circle One)

Model Number ________________

Element	Wavelength (nm)	MDL (ug/L)	IDL (ug/L)	Element	Wavelength (nm)	MDL (ug/L)	IDL (ug/L)
1. Aluminum		200		13. Magnesium		5000	
2. Antimony		150		14. Manganese		15	
3. Arsenic		250		15. Mercury		NR	
4. Barium		200		16. Nickel		40	
5. Beryllium		5		17. Potassium		5000	
6. Cadmium		20		18. Selenium		400	
7. Calcium		5000		19. Silver		30	
8. Chromium		10		20. Sodium		5000	
9. Cobalt		50		21. Thallium		200	
10. Copper		25		22. Vanadium		50	
11. Iron		100		23. Zinc		20	
12. Lead		200					

Footnotes:
- Indicate the instrument for which the IDL applies with a "P" (for ICP), an "A" (for Flame AA), an "F" (for Furnace AA), or a "CV" (for Cold Vapor AA) behind the IDL value.
- Indicate elements commonly run with background correction (AA) with a "B" behind the analytical wavelength.
- If more than one ICP/Flame or Furnace AA is used, submit separate Forms XI-XIII for each instrument.

Comments: ____

Lab Manager ____________________

Figure 11. Instrument Detection Limits — ICP/AA

Form XIb (Quarterly)
INSTRUMENT DETECTION LIMITS - Furnace/Cold Vapor AA

LAB NAME ____________________ DATE ____________________

Furnace/Cold

Vapor AA Model Numbers__________

Element	Wavelength (nm)	MDL (ug/L)	IDL (ug/L)	Element	Wavelength (nm)	MDL (ug/L)	IDL (ug/L)
1. Aluminum		NR		13. Magnesium		NR	
2. Antimony		60		14. Manganese		NR	
3. Arsenic		10		15. Mercury		0.2	
4. Barium		NR		16. Nickel		NR	
5. Beryllium		NR		17. Potassium		NR	
6. Cadmium		5		18. Selenium		5	
7. Calcium		NR		19. Silver		10	
8. Chromium		NR		20. Sodium		NR	
9. Cobalt		NR		21. Thallium		10	
10. Copper		NR		22. Vanadium		NR	
11. Iron		NR		23. Zinc		NR	
12. Lead		5					

Footnotes:
- o Indicate the instrument for which the IDL applies with a "P" (for ICP), an "A" (for Flame AA), an "F" (for Furnace AA), or a "CV" (for Cold Vapor AA) behind the IDL value.
- o Indicate elements commonly run with background correction (AA) with a "B" behind the analytical wavelength.
- o If more than one ICP/Flame or Furnace AA is used, submit separate Forms XI-XIII for each instrument.

Comments: ____

____

____

Lab Manager ____________________

Figure 12. Instrument Detection Limits — Furnace/Cold Vapor AA

Form XII (Quarterly)
ICP INTERELEMENT CORRECTION FACTORS

LABORATORY NAME ____________ ICP MODEL NUMBER ____________

DATE ____________

		Interelement Correction Factors for							
Analyte	Analyte Wavelength (nm)	Al	Ca	Fe	Mg				
1. Antimony									
2. Arsenic									
3. Barium									
4. Beryllium									
5. Cadmium									
6. Chromium									
7. Cobalt									
8. Copper									
9. Lead									
10. Manganese									
11. Mercury									
12. Nickel									
13. Potassium									
14. Selenium									
15. Silver									
16. Sodium									
17. Thallium									
18. Vanadium									
19. Zinc									

Comments: ____________

Lab Manager ____________

Figure 13. ICP Interelement Correction Factors

Form XII (Quarterly) (Cont'd)
ICP INTERELEMENT CORRECTION FACTORS

LABORATORY NAME ____________ ICP MODEL NUMBER ____________

DATE ____________

		Interelement Correction Factors for							
Analyte	Analyte Wavelength (nm)								
1. Antimony									
2. Arsenic									
3. Barium									
4. Beryllium									
5. Cadmium									
6. Chromium									
7. Cobalt									
8. Copper									
9. Lead									
10. Manganese									
11. Mercury									
12. Nickel									
13. Potassium									
14. Selenium									
15. Silver									
16. Sodium									
17. Thallium									
18. Vanadium									
19. Zinc									

Comments: ____________

Lab Manager ____________

Figure 14. ICP Interelement Correction Factors (Continued)

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Form XIII (Quarterly)
ICP LINEAR RANGES

LAB NAME ____________________ ICP MODEL NUMBER __________

DATE ____________________

Analyte	Integration Time (Seconds)	Concentration (ug/L)	Analyte	Integration Time (Seconds)	Concentration (ug/L)
1. Aluminum			13. Magnesium		
2. Antimony			14. Manganese		
3. Arsenic			15. Mercury		
4. Barium			16. Nickel		
5. Beryllium			17. Potassium		
6. Cadmium			18. Selenium		
7. Calcium			19. Silver		
8. Chromium			20. Sodium		
9. Cobalt			21. Thallium		
10. Copper			22. Vanadium		
11. Iron			23. Zinc		
12. Lead					

Footnotes: o Indicate the elements not determined by ICP with the notation "NA".

Comments: ____________________

____

____

Lab Manager ____________________

Figure 15. ICP Linear Ranges

DETERMINATION OF METALS BY FURNACE ATOMIC ABSORPTION SPECTROPHOTOMETRY

1.0 SCOPE AND APPLICATION

1.1 Dissolved elements are determined in filtered and acidified samples. Appropriate steps must be taken in all analyses to ensure that potential interferences are taken into account. This is especially true when samples contain high dissolved solids. (See Section 3.0.)

1.2 Total elements are determined after appropriate digestion procedures are performed. Since digestion techniques increase the dissolved solids content of the samples, appropriate steps must be taken to correct for potential interference effects. (See Section 3.0.)

1.3 Detection limits, sensitivity and optimum ranges of the metals will vary with the various makes and models of satisfactory atomic absorption spectrophotometers. The data shown in Table 1, however, provide some indication of the detection limits and concentration ranges measurable using furnace techniques. The concentration ranges given in Table 1 are somewhat dependent upon equipment such as the type of spectrophotometer and furnace accessory, the energy source and the degree of electrical expansion of the output signal. When using furnace techniques, however, the analyst should be cautioned as to possible chemical reactions occurring at elevated temperatures which may result in either suppression or enhancement of the analysis element. To ensure valid data with furnace techniques, the analyst must examine each matrix for interference effects (see Section 3.1.1) and if detected, treat accordingly using either successive dilution, matrix modification or method of standard additions.

1.4 Because of the differences between various makes and models of satisfactory instruments, no detailed instrumental operating instructions can be provided. Instead, the analyst is referred to the instructions provided by the manufacturer of the particular instrument.

Table 1. Furnace AA Detection Limits and Concentration Ranges

Element	Wavelength (nm)	Approximate Detection Limit[a] (ug/L)	Optimum Concentration Range[a] (ug/L)
Antimony	217.6	3	20-300
Arsenic	193.7	1	5-100
Cadmium	228.8	0.1	0.5-10
Lead	283.3	1	5-100
Selenium	196.0	2	5-100
Silver	328.1	0.2	1-25
Thallium	276.8	1	5-100

a. Using a 20-L sample.

2.0 SUMMARY OF METHOD

2.1 When using the furnace technique in conjunction with an atomic absorption spectrophotometer, a representative aliquot of a sample is placed in the graphite tube in the furnace, evaporated to dryness, charred, and atomized. Analyte atoms are vaporized and dissociated for absorption in the tube. The use of small sample volumes or detection of low concentrations of element is possible. Radiation from a light source, hollow cathode or electrodeless discharge lamp of the element being determined is passed through the vapor containing ground-state atoms of that element. The intensity of the transmitted radiation decreases in proportion to the amount of the ground state element in the vapor.

The metal atoms to be measured are placed in the beam of radiation by increasing the temperature of the furnace thereby causing the injected specimen to become volatilized. A monochromator isolates the characteristic radiation from the hollow cathode lamp and a photosensitive device measures the attenuated transmitted radiation.

2.2 Although methods have been reported for the analysis of solids by atomic absorption spectroscopy (Spectrochim Acta, 24B 53, 1969) the technique generally is limited to metals in solution or solubilized through some form of sample processing.

2.2.1 Preliminary treatment of wastewater and/or industrial effluents is usually necessary because of the complexity and variability of the sample matrix. Suspended material must be subjected to a solubilization process before analysis. This process may vary because of the metals to be determined and the nature of the sample being analyzed. When the breakdown of organic material is necessary, the process should include a wet digestion with nitric acid.

2.2.2 In those instances where complete characterization of a sample is desired, the suspended material must be analyzed separately. This may be accomplished by filtration and acid digestion of the suspended material. Metallic constituents in this acid digest are subsequently determined and the sum of the dissolved plus suspended concentrations will then provide the total concentrations present. The sample should be filtered as soon as possible after collection and the filtrate acidified immediately.

2.2.3 The total sample may also be treated with acid without prior filtration to measure what may be termed "total recoverable" concentrations.

3.0 INTERFERENCES

3.1 Flameless Atomization

3.1.1 Although the problem of oxide formation is greatly reduced with furnace procedures because atomization occurs in an inert atmosphere, the technique is still subject to chemical and matrix interferences. The composition of the sample matrix can have a major effect on the analysis. It is those effects which must be determined and taken into consideration in the analysis of each different matrix encountered. To help verify the absence of matrix or chemical interference, use the following procedure. Withdraw from the sample two equal aliquots. To one of the aliquots add a known amount of analyte and dilute both aliquots to the same predetermined volume. (The dilution volume should be based on the analysis of the undiluted sample. Preferably, the dilution should be 1 + 3 while keeping in mind the optimum concentration range of the analysis. Under no circumstances should the dilution be less than 1 + 1.) The diluted aliquots should then be analyzed and the unspiked results multiplied by the dilution factor should be compared to the original determination. Agreement of the results (within ±10 percent) indicates the absence of interference. Comparison of the actual signal from the spike to the expected response from the analyte in an aqueous standard should help confirm the finding from the dilution analysis. Those samples which indicate the presence of interference should be treated in one or more of the following ways.

3.1.1.1 The samples should be successively diluted and re-analyzed to determine if the interference can be eliminated.

3.1.1.2 The matrix of the sample should be modified in the furnace. Examples are the addition of ammonium nitrate to remove alkali chlorides, ammonium phosphate to retain cadmium, and nickel nitrate for arsenic and selenium analyses (Atomic Absorption Newsletter Vol. 14, No. 5, p. 127, Sept.-Oct. 1975). The mixing of hydrogen with the inert purge gas has also been used to suppress chemical interference. The hydrogen acts as a reducing agent and aids in molecular dissociation.

3.1.1.3 Analyze the sample by method of standard additions while noting the precautions and limitations of its use.

3.1.2 Gases generated in the furnace during atomization may have molecular absorption bands encompassing the analytical wavelength. When this occurs, either the use of background correction or choosing an alternative wavelength outside the absorption band should eliminate this interference. Nonspecific broad band absorption interference can also be compensated for with background correction.

3.1.3 Interference from a smoke-producing sample matrix can sometimes be reduced by extending the charring time at a higher temperature or utilizing an ashing cycle in the presence of air. Care must be taken, however, to prevent loss of the analysis element.

3.1.4 Samples containing large amounts of organic materials should be oxidized by conventional acid digestion prior to being placed in the furnace. In this way broad band absorption will be minimized.

3.1.5 From anion interference studies in the graphite furnace, it is generally accepted that nitrate is the preferred anion. Therefore, nitric acid is preferable for any digestion or solubilization step. If another acid in addition to HNO_3 is required, a minimum amount should be used. This applies particularly to hydrochloric and to a lesser extent to sulfuric and phosphoric acids.

3.1.6 Carbide formation resulting from the chemical environment of the furnace has been observed with certain elements that form carbides at high temperatures. Molybdenum may be cited as an example. When this takes place, the metal will be released very slowly from the carbide as atomization continues. For molybdenum, one may be required to atomize for 30 s or more before the signal returns to baseline levels. This problem is greatly reduced and the sensitivity increased with the use of pyrolytically-coated graphite.

3.1.7 Ionization interferences have, to date, not been reported with furnace techniques.

3.1.8 Although quite rare, spectral interference can occur when an absorbing wavelength of an element present in the sample, but not being determined, falls within the width of the absorption line of the element of interest. The results of the determination will then be erroneously high, due to the contribution of the interfering element to the atomic absorption signal. Also, interference can occur when resonant energy from another element in a multi-element lamp or a metal impurity in the lamp cathode falls within the bandpass of the slit setting, and that metal is present in the sample. This type of interference may sometimes be reduced by narrowing the slit width.

3.1.9 Contamination of the sample can be a major source of error because of the extreme sensitivities achieved with the furnace. The sample preparation work area should be kept scrupulously clean. All glassware should be cleaned as directed in Section 7.7. Pipet tips have been known to be a source of contamination. If suspected, they should be acid soaked with 1:5 HNO_3 and rinsed thoroughly with tap and deionized water. The use of a better grade pipet tip can greatly reduce this problem. It is very important that special attention be given to reagent blanks in both analysis and the correction of analytical results. Lastly, pyrolytic graphite, because of the production process and handling, can become contaminated. As many as five to possibly ten high temperature burns may be required to clean the tube before use.

4.0 DEFINITIONS

4.1 Dissolved - Those elements which will pass through a 0.45-um membrane filter.

4.2 Suspended - Those elements which are retained by a 0.45-um membrane filter.

4.3 Total - The concentration determined on an unfiltered sample following vigorous digestion.

4.4 Instrumental detection limits - The instrumental detection limits are determined by multiplying by three the average of the standard deviation obtained from the analysis of a standard solution at a concentration 3 to 5 times the instrument detection limits.

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4.5 Sensitivity - The slope of the analytical curve; i.e., functional relationship between absorbance and concentration. In atomic absorption spectrophotometry the sensitivity is defined as the concentration of an element in mg/L that produces an absorption of 1 percent.

4.6 Instrument check standard - A standard of known concentration prepared by the analyst to monitor and verify instrument performance on a daily basis. (See Section 8.5.1.)

4.7 Quality control sample - A solution obtained from an outside source having known concentration values to be used to verify the calibration standards. (See Section 8.5.2.)

4.8 Optimum Concentration Range - A range, defined by limits expressed in concentration, below which scale expansion must be used and above which curve correction should be considered. This range will vary with the sensitivity of the instrument and the operating condition employed.

4.9 Reagent blank - A volume of deionized, distilled water containing the same acid matrix as the calibration standards carried through the entire analytical scheme. (See Section 8.4.2.)

4.10 Calibration blank - A volume of deionized, distilled water acidified with HNO_3 and HCl. (See Section 8.4.1.)

4.11 Method of standard addition - The standard addition technique involves the use of the unknown and the unknown-plus-a-known amount of standard by adding known amounts of standard to one or more aliquots of the processed sample solution.

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

5.1 For the determinations of trace elements, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. Sample containers can introduce either positive or negative errors in the measurement of trace elements by (a) contributing contaminants through leaching or surface desorption and (b) by depleting concentrations through adsorption. Thus, the collection and treatment of the sample prior to analysis requires particular attention. Laboratory glassware including the sample bottle (whether polyethylene, polypropylene or FEP-fluorocarbon) should be thoroughly washed with detergent and tap water, rinsed with nitric acid (1+1), tap water, hydrochloric acid (1+1), tap and finally deionized, distilled water in that order (see Notes 1 and 2).

Note 1: Chromic acid may be useful to remove organic deposits from glassware; however, the analyst should be cautioned that the glassware must be thoroughly rinsed with water to remove the last traces of chromium. This is especially important if chromium is to be included in the analytical scheme. A commercial product, NOCHROMIX, available from Godax Laboratories, 6 Varick St., New York, NY, 10013, may be used in place of chromic acid. Chromic acid should not be used with plastic bottles.

Note 2: If it can be documented through an active analytical quality control program using spiked samples and reagent blanks, that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure.

5.2 In the collection of samples it is important to perform sample preservation.

5.2.1 Aqueous samples collected for the determination of total elements are not to be filtered. The sample should be acidified with HNO_3 (1 + 1) to a pH of 2 or less. Normally, 3 mL of HNO_3 (1 + 1) per liter should be sufficient to preserve the sample.

5.2.2 Aqueous samples collected for the determination of dissolved elements must be filtered through a 0.45-um membrane filter immediately on site before adding preservative. (Glass or plastic filtering apparatus are recommended to avoid possible contamination.) Use the first 50 to 100 mL to rinse the filter flask. Discard this portion and collect the required volume of filtrate. Acidify the filtrate with HNO_3 (1 + 1) to a pH of 2 or less. Normally, 3 mL of HNO_3 (1 + 1) per liter should be sufficient to preserve the sample.

5.2.3 Solid samples collected for the determination of total metals should be mixed thoroughly to achieve homogeneity. Solid samples should be preserved by maintaining them at 4°C for and during shipment to the laboratory. Samples must be refrigerated upon receipt at the laboratory until analysis.

6.0 SAFETY

6.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material handling data sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified (7,8,9) for the information of the analyst.

7.0 APPARATUS AND EQUIPMENT

7.1 Atomic absorption spectrophotometer - Single or dual channel, single- or double-beam instruments having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, a background corrector, and provisions for interfacing with a strip chart recorder. In addition, the instrument should have either a peak height or peak area mode.

7.2 Hollow cathode lamps - Single element lamps are to be preferred but multi-element lamps may be used. Electrodeless discharge lamps may also be used when available.

7.3 Graphite furnace - Any furnace device capable of reaching the specified temperatures is satisfactory.

7.4 Strip chart recorder - A recorder is strongly recommended for furnace work so that there will be a permanent record and any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can be easily recognized.

7.5 Pipets - 5 to 100 uL as required, with disposable tips.

Note: Pipet tips which are white in color, do not contain CdS, and have been found suitable for research work are available from Ulster Scientific, Inc., 53 Main St., Highland, NY 12528 (914) 691-7500.

7.6 Pressure-reducing valves - The supplies of the furnace gas shall be maintained at pressures somewhat higher than the controlled operating pressure of the instrument by suitable valves.

7.7 Glassware - All glassware, linear polyethylene, polypropylene or Teflon containers, including sample bottles should be washed with detergent, rinsed with tap water, HNO_3 (1 + 1) tap water, HCl

(1 + 1), tap water and deionized, distilled water in that order. (See Notes 1 and 2 in Section 5.0 concerning the use of chromic acid and the cleaning procedure.)

7.8 Argon or nitrogen gas supply - Welding grade or better.

8.0 REAGENTS

8.1 Acids in the preparation of standards and for sample processing must be ultra-high purity grade or equivalent. Redistilled acids are acceptable.

8.1.1 Acetic acid (sp gr 1.19) - Concentrated.

8.1.2 Hydrochloric acid (sp gr 1.19) - Concentrated.

8.1.3 Hydrochloric acid (1 + 1) - Add 500 mL of concentrated HCL (sp gr 1.19) to 400 mL of deionized, distilled water and dilute to 1 L.

8.1.4 Nitric acid (sp gr 1.41) - Concentrated.

8.1.5 Nitric acid (1 + 1) - Add 500 mL of concentrated HNO_3 (sr gr 1.41) to 400 mL of deionized, distilled water and dilute to 1 L.

8.2 Deionized, distilled water - Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use deionized, distilled water for the preparation of all reagents, calibration standards and as dilution water. The purity of this water must be equivalent to ASTM Type II reagent water.

8.3 Stock solutions and calibration standards - Standard stock solutions may be purchased or prepared from ultra-high purity grade chemicals or metals. All salts must be dried for 1 h at 105° unless otherwise specified. Ultra-high purity is defined as 5-9s or better grade chemicals or metals.

(Caution: Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.)

Typical stock solution preparation procedures follow:

8.3.1 Antimony

8.3.1.1 Antimony stock solution (1000 mg/L) - Carefully weigh 2.7426 g of antimony potassium tartrate (analytical reagent grade) and dissolve in deionized, distilled water. Dilute to 1 L with deionized water.

8.3.1.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

8.3.2 Arsenic

8.3.2.1 Arsenic stock solution (1000 mg/L) - Dissolve 1.320 g of arsenic trioxide, As_2O_3 (analytical reagent grade) in 100 mL of deionized, distilled water containing 4 g of NaOH. Acidify the solution with 20 mL of concentrated HNO_3 and dilute to 1 L.

8.3.2.2 Nickel nitrate solution (5 percent) - Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2.6H_2O$ in deionized, distilled water and make up to 100 mL.

8.3.2.3 Nickel nitrate solution (1 percent) - Dilute 20 mL of the 5 percent nickel nitrate solution to 100 mL with deionized, distilled water.

8.3.2.4 Arsenic calibration solution - Prepare dilutions of the arsenic stock solution to be used as calibration standards at the time of analysis. Withdraw appropriate aliquots of the stock solution, add 1 mL of concentrated HNO_3, 2 mL of 30 percent H_2O_2 and 2 mL of the 5 percent nickel nitrate solution. Dilute to 100 mL with deionized, distilled water.

8.3.3 Cadmium

8.3.3.1 Cadmium stock solution (1000 mg/L) - Carefully weigh 2.28 g of cadmium sulfate, $3CdSO_4.8H_2O$ (analytical reagent grade), and dissolve in deionized, distilled water. Make up to 1 L with deionized, distilled water.

8.3.3.2 Ammonium phosphate solution (4 percent) - Dissolve 4 grams of ammonium phosphate $(NH_4)_2HPO_4$ (analytical reagent grade) in deionized, distilled water and dilute to 100 mL.

8.3.3.3 Prepare dilutions of stock cadmium solution to be used as calibration standards at the time of analysis. To each 100 mL of standard and sample alike add 2.0 mL of the ammonium phosphate solution. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

8.3.4 Lead

8.3.4.1 Lead stock solution (1000 mg/L) - Carefully weigh 1.5999 g of lead nitrate, $Pb(NO_3)_2$ (analytical reagent grade), and dissolve in deionized, distilled water. When solution is complete, acidify with 10 mL of redistilled HNO_3 and dilute to 1 L with deionized, distilled water.

8.3.4.2 Lanthanum nitrate solution - Dissolve 58.64 g of ACS reagent grade La_2O_3 in 100 mL concentrated calibration standards HNO_3 and dilute to 1000 mL with deionized, distilled water.

8.3.4.3 Lead concentrated calibration standards - Prepare dilutions of stock lead solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation. To each 100 mL of diluted standard, add 10 mL of the lanthanum nitrate solution.

8.3.5 Selenium

8.3.5.1 Selenium stock solution (1000 mg/L) - Dissolve 0.3453 g of selenous acid (actual assay 94.6 percent H_2SeO_3) in deionized, distilled water and make up to 200 mL.

8.3.5.2 Nickel nitrate solution (5 percent) - Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2.6H_2O$ in deionized, distilled water and make up to 100 mL.

8.3.5.3 Nickel nitrate solution (1 percent) - Dilute 20 mL of the 5 percent nickel nitrate to 100 mL with deionized, distilled water.

8.3.5.4 Selenium calibration standards - Prepare dilutions of selenium solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation. Withdraw appropriate aliquots of the stock solution, add 1 mL of concentrated HNO_3, 2 mL of 30 percent H_2O_2, and 2 mL of the 5 percent nickel nitrate solution. Dilute to 100 mL with deionized, distilled water.

8.3.6 Silver

8.3.6.1 Silver stock solution (1000 mg/L) - Dissolve 1.575 g of $AgNO_3$ (analytical reagent grade) in deionized, distilled water. Add 10 mL of concentrated HNO_3 and make up to 1 L.

8.3.6.2 Prepare dilutions of silver stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

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8.3.7 Thallium

8.3.7.1 Thallium stock solution (1000 mg/L) - Dissolve 1.303 g of thallium nitrate, $Tl\ NO_3$ (analytical reagent grade), in deionized, distilled water. Add 10 mL of concentrated nitric acid and dilute to 1 L with deionized, distilled water.

8.3.7.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

8.4 Two types of blanks are required for the analysis. The calibration blank (Section 4.10) is used in establishing the analytical curve while the reagent blank (Section 4.9) is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

8.4.1 The calibration blank is prepared by diluting 2 mL of HNO_3 (1 + 1) to 100 mL with deionized, distilled water.

8.4.2 The reagent blank must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

8.5 In addition to the calibration standards, an instrument check standard (Section 4.6) and a quality control sample (Section 4.7) are also required for the analyses.

8.5.1 The instrument check standard for continuing calibration verification is prepared by the analyst by combining

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compatible elements at a concentration equivalent to the mid-point of their respective calibration curves (Section 13.1.3) or the initial calibration verification solution (Section 13.1.1) may be used.

8.5.2 The quality control sample for the initial calibration verification should be prepared in the same acid matrix as the calibration standards and in accordance with the instructions provided by the supplier. EPA will either supply a quality control sample or information where one of equal quality can be procured (Section 13.1.1).

9.0 CALIBRATION

9.1 Calibration Standards - Because of the differences in the response of the various instrument configurations and in the selection of analytical wavelengths, no specific concentration can be provided. Instead, the analyst should establish the appropriate calibration standard concentration for each individual analyte line on that particular instrument.

9.2 Instrument Operating Conditions - Because of the differences between various makes and models of satisfactory instruments, the analyst should follow the instructions provided by the manufacturer of the particular instrument. Suggested operating conditions are listed in Table 2. Sensitivity, instrumental detection limit, precision, and optimum concentration range must be investigated and established for each individual analyte line on a particular instrument. All measurements must be within the optimum concentration range. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions used satisfy the analytical requirements and to maintain quality control data confirming instrument performance and analytical results. Background corrections are required for all furnace AA measurements.

Table 2. Suggested Operating Conditions[a,b,c,d]

	Drying		Ashing		Atomizing			
	Time (s)	Temperature (°C)	Time (s)	Temperature (°C)	Time (s)	Temperature (°C)	Purge Gas Atmosphere	Wavelength (nm)
Antimony[f]	30	125	30	800	10	2700	argon[e]	217.6
Arsenic[g]	30	125	30	1100	10	2700	argon	193.7
Cadmium[h]	30	125	30	500	10	1900	argon	228.8
Lead[i,j]	30	125	30	500	10	2700	argon	283.3[k]
Selenium[l]	30	125	30	1200	10	2700	argon	196.0
Silver[m]	30	125	30	400	10	2700	argon	328.1
Thallium	30	125	30	400	10	2400	argon[e]	276.8

a. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, purge gas interrupt and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

b. For every sample analyzed, verification is necessary to determine that method of standard addition is not required (see Section 13.0).

c. If method of standard addition is required, follow the procedure given in Section 13.0.

d. The use of background correction is required.

e. Nitrogen may also be used as the purge gas.

f. If chloride concentration presents a matrix problem or causes a loss previous to atomization, add an excess 5 mg of ammonium nitrate to the furnace and ash using a ramp accessory or with incremental steps until the recommended ashing temperature is reached.

g. The use of the electrodeless discharge lamps for the light source is recommended.

Table 2. Suggested Operating Conditions[a,b,c,d] (Continued)

h. Contamination from the work area is critical in cadmium analysis. Use pipet tips which are free of cadmium.

i. To suppress sulfate interference (up to 1500 ppm) lanthanum is added as the nitrate to both samples and calibration standards. (Atomic Absorption Newsletter Vol. 15, No. 3, p. 71, May-June 1976.)

j. Since glassware contamination is a severe problem in lead analysis, all glassware should be cleaned immediately prior to use, and once cleaned, should not be open to the atmosphere except when necessary.

l. Selenium analysis suffers interference from chlorides (>800 mg/L) and sulfate (>200 mg/L). For the analysis of industrial effluents and samples with concentrations of sulfate from 200 to 2000 mg/L, both samples and standards should be prepared to contain 1 percent nickel.

m. The use of halide acids should be avoided.

10.0 PROCEDURE

10.1 Aqueous Samples

10.1.1 For the determination of arsenic, cadmium, lead, selenium, silver, and thallium in aqueous samples, shake sample and transfer 100 mL of a well mixed sample to a 250-mL beaker. Add 1 mL of HNO_3 (1 + 1) and 2 mL of 30 percent H_2O_2 to the sample cover with watch glass or similar cover and heat on a steam bath or hot plate for 2 h at 95°C or until the volume has been reduced to between 25 and 50 mL making certain the sample does not boil. After this treatment, cool sample and filter to remove insoluble material that could clog the nebulizer. (See Note 3.) Adjust the volume to 100 mL with deionized, distilled water. The sample is now ready for analysis.

Concentrations so determined shall be reported as "total."

Note 3: In place of filtering, the sample after dilution and mixing may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

10.1.2 For the determination of antimony in aqueous samples, shake sample and transfer 100 mL of a well-mixed sample to a 250-mL beaker. Add 2 mL of HNO_3 (1 + 1) and 10 mL of HCl (1 + 1) to the sample. Cover with watch glass or similar cover and heat on a steam bath or hot plate for 2 h at 95°C or until the volume has been reduced to between 25 and 50 mL making certain the sample does not boil. After this treatment, cool sample and filter to remove insoluble material that could clog the nebulizer. (See Note 3.) Adjust the volume to 100 mL with deionized, distilled water. The sample is now ready for analysis.

Concentrations so determined shall be reported as "total."

10.2 Solid Samples

10.2.1 For the determination of arsenic, cadmium, lead, selenium, silver, and thallium in solid samples, e.g., sediments, sludges, and soils, mix the sample thoroughly to achieve homogeneity. For each digestion procedure, weigh (to the nearest 0.01 g) a 1.0 to 1.5-g portion of sample and transfer to a 100-mL beaker.

Add 10mL of HNO_3 (1 + 1), mix the slurry, and cover with a watch glass. Heat the sample to $95^{\circ}C$ and reflux for 10 min without boiling. Allow the sample to cool, add 5 mL of concentrated HNO_3, replace the watch glass, and reflux for 30 min. Do not allow the volume to be reduced to less than 5 mL while maintaining a covering of solution over the bottom of the beaker.

After the second reflux step has been completed and the sample has cooled, add 2 mL of Type II water and 3 mL of 30 percent hydrogen peroxide (H_2O_2). Return the beaker to the hot plate for warming to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides, and cool the beaker.

Continue to add 30 percent H_2O_2 in 1-mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged. (Note: Do not add more than a total of 10 mL of 30 percent H_2O_2). Continue heating the acid-peroxide digestate until the volume has been reduced to approximately 2 mL, then add 10 mL of Type II water, and warm the mixture. After cooling, filter through Whatman No. 42 filter paper (or equivalent - see Note 1), and dilute to 100 mL with Type II water (or centrifuge the sample). The diluted digestate solution contains approximately 2 percent (v/v) HNO_3. Dilute the digestate to 200 mL with deionized water. For analysis, withdraw aliquots of appropriate volume and add the required reagent or matrix modifier listed below.

1. Arsenic - Add 100 uL of the 5 percent nickel nitrate solution to 5 mL of the digested sample. The sample is now ready for injection into the furnace.

2. Cadmium - No reagent or matrix modifier required.

3. Lead - Add 10 mL of the lanthanum nitrate solution to each 100 mL of prepared sample solution.

4. Selenium - Add 100 uL of the 5 percent nickel nitrate solution to 5 mL of the digested sample. The sample is now ready for injection into the furnace.

5. Silver - No reagent or matrix modifier required.

6. Thallium - No reagent or matrix modifier required.

10.2.2 For the determination of antimony in solid samples, e.g., sediments, sludges, and soils, mix the sample thoroughly to achieve homogeneity. For each digestion procedure, weigh (to the nearest 0.01 g) a 1.0 to 1.5-g portion of sample and transfer to a 100-mL beaker.

Add 10 mL of HNO_3 (1 + 1), mix the slurry, and cover with a watch glass. Heat the sample to 95°C and reflux for 10 min without boiling. Allow the sample to cool, add 5 mL of concentrated HNO_3, replace the watch glass, and reflux for 30 min. Do not allow the volume to be reduced to less than 5 mL while maintaining a covering of solution over the bottom of the beaker.

After the second reflux step has been completed and the sample has cooled, add 2 mL of Type II water and 3 mL of 30 percent hydrogen peroxide (H_2O_2). Return the beaker to the hot plate for warming to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides, and cool the beaker. Continue to add 30 percent H_2O_2 in 1-mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged. (Note: Do not add more than a total of 10 mL 30 percent H_2O_2.)

Next, add 5 mL of HCl (1 + 1) and 10 mL of Type II water, return the covered beaker to the hot plate, and heat for an additional 10 min. After cooling, filter through Whatman No. 42 filter paper (or equivalent, or centrifuge the sample - see Note 3). Dilute the digestate to 200 mL (final volume) with deionized water. The sample is now ready for analysis.

11.0 CALCULATIONS

11.1 Reagent blanks should be analyzed for each Case and used in all analyses to ascertain whether sample concentrations reflect contamination in the following manner:

11.1.1 If the concentration of the blank is less than or equal to the instrument detection level, no correction of sample results is performed.

11.1.2 If the concentration of the blank is above the instrument detection level for any group of samples associated with a particular blank, the concentration of the sample with the least concentrated analyte must be 10 times the blank concentration, or all samples associated with the blank and less than 10 times the blank concentration must be redigested and re-analyzed, with the exception of an identified aqueous-blank value and the fact that a blank concentration was observed documented in the Case Narrative.

11.2 If dilutions were performed, the appropriate factor must be applied to sample values.

11.3 A separate determination of percent solids must be performed (Figure 1).

11.3.1 The concentrations determined in the digest for solid samples are to be reported on the basis of the dry weight of the sample.

$$\text{Concentration (dry wt.) (mg/kg)} = \frac{C \times V}{W \times S}$$

where:

C = Concentration (mg/L)

V = Final volume after sample preparation (L)

W = Weight of wet sample (Kg)

S = Percent solids/100.

12.0 REPORTING

12.1 All reports in the sample data package must be submitted in a legible form. The data report package for furnace AA analyses of each sample must be complete before submission and shall include:

12.1.1 The cover page for the DOE Environmental Survey Inorganic Analysis Data Package (see Figure 2) including DOE/ES and laboratory cross reference numbers, Case Narrative (comments), and footnotes used in the data package.

12.1.2 Tabulated results in ug/L for aqueous samples or mg/kg for solid samples (identification and quantity) of specified chemical constituents (Table 1) by the specified analyses validated and signed in original signature by the Laboratory Manager, and reported on Form I (Figure 3). The results for solid samples will be reported on a dry-weight basis. Percent solids are not required on aqueous samples. If the value or the result is greater than or equal to the Instrument Detection Limit (IDL), corrected for dilutions, report the value. All dilutions not required by the contract and affecting the IDL, must be noted on an element by element basis on Form I. If the value is less than the Contract Required Detection Limits (CRDL) in Table 3, put the value in brackets (e.g., [10]). If the element was analyzed for but not detected, report the instrument detection limit value with a "U" (e.g., 10U). If the duplicate sample analysis is not within the control limits, flag it with an asterisk(*). Note any sample problems in the Case Narrative. Report results to two significant figures for values from 0 to 100 and three significant figures for results greater than 100. For rounding rules, follow the EPA Handbook of Analytical Quality Control in Water and Wastewater Laboratories (EPA-600/4-79-019).

12.1.3 The duplicate sample analysis results should be reported on Form VI (Figure 4) and included in the data package.

12.1.4 The method of standard addition results should be reported on Form VIII (Figure 5) and included in the data package.

12.1.5 If furnace AA data are to be reported following the U.S. EPA CLP format, the additional forms required in the data package include Form II, Form III, Form V, Form VII, and Form XI (Figures 6-10).

13.0 QUALITY ASSURANCE/QUALITY CONTROL

13.1 This section outlines the minimum quality assurance/quality control (QA/QC) operations necessary to satisfy the analytical requirements of the method. The following QA/QC operations must be performed as stated:

13.1.1 Initial Calibration and Calibration Verification.

13.1.2 Continuing Calibration Verification.

13.1.3 Preparation Blank Analysis.

13.1.4 Matrix Spike Analysis.

13.1.5 Duplicate Sample Analysis.

13.1.6 Furnace AA QC Analysis (Method of Standard Additions may be required under certain conditions.)

13.1.7 Laboratory Quality Control Sample Analysis.

13.2 Check the instrument standardization by analyzing appropriate quality control check standards as follows.

13.2.1 A quality control sample (Section 8.5.2) must be used daily for the initial calibration verification. If the Initial Calibration Verification Solution(s) are not available from EPA, or where a certified solution of an analyte is not available from any source, analyses shall be conducted on an independent standard at a concentration other than that used for calibration, but within the calibration range. An independent standard is defined as a standard composed of the analytes from a different source than those used in the standards for the initial calibration. When measurements exceed the control limits of ±10 percent, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified.

13.2.2 Analyze the calibration blank (Section 8.5.1) at a frequency of 10 percent. The result should be within ±5 times the experimentally determined instrument detection limit. If the result is not within the control level, terminate the analysis, correct the problem and recalibrate the instrument.

13.2.3 For continuing calibration verification, analyze an appropriate instrument check standard (Section 8.6.1) containing the elements of interest at a frequency of 10 percent. This check standard is used to determine instrument drift. If agreement is not within ±10 percent of the expected values, the analysis is out of control. The analysis must be terminated, the problem corrected, the instrument recalibrated, and the preceding 10 samples re-analyzed.

13.2.4 The spiked sample analysis is designed to provide information about the effect of the sample matrix on the digestion and measurement methodology. The spike is added before the digestion steps. At least one spiked sample analysis must be performed on each group of samples of a similar matrix type (i.e., water, soil) and concentration (i.e., low, medium) for each Case of samples or for each 20 samples received, whichever is more frequent. Samples identified as field blanks cannot be used for spiked sample analysis. The analyte spike must be added in the amount given in Table 4 for each element analyzed. If the spike recovery is not within the limits of 75 to 125 percent, the data of all samples received associated with that spiked sample must be flagged with the letter "N" on Forms I and V (Figures 3 and 8). An exception to this rule is granted in situations where the sample concentration exceeds the spike concentration by a factor of four or more. In such a case, the spike recovery should not be considered and the data shall be reported unflagged even if the percent recovery does not meet the 75 to 125 percent recovery criteria. In the instance where there is more than one spiked sample per matrix per Case, if one spike sample recovery is not within contract criteria, flag all the samples of the same matrix in the Case. Individual component percent recoveries are calculated using the following equation.

$$\text{Percent recovery} = \frac{(\text{SSR}-\text{SR})}{\text{SA}} \times 100$$

where:

SSR = Spiked sample result

SR = Sample result

SA = Spike added.

Table 3. Elements Determined by Furnace Atomic Absorption Spectrophotometry

Element	Contract Required Detection Level (ug/L)
Antimony	60
Arsenic	10
Cadmium	5
Lead	5
Selenium	5
Silver	10
Thallium	10

13.2.5 At least one duplicate sample must be analyzed from each group of samples of a similar matrix type (i.e., water, soil) and concentration (i.e., low, medium) for each Case of samples or for each 20 samples received, whichever is more frequent. Samples identified as field blanks cannot be used for duplicate sample analysis. The relative percent differences (RPD) for each component are calculated using the following equation.

$$RPD = \frac{|D_1 - D_2|}{(D_1 + D_2)/2} \times 100$$

where:

D1 = First sample value
D2 = Second sample value (duplicate).

The results of the duplicate sample analysis must be reported on Form VI (Figure 4). A control limit of ±20 percent for RPD shall be used for sample values greater than 5 times the CRDL. A control limit of ± the CRDL shall be used for sample values less than 5 times the CRDL (Table 2), and this control limit (±CRDL) should be entered in the "Control Limit" column of Form VI. If one result is above the 5 times CRDL level and the other is below use the ± CRDL criteria. If either sample value is less than the CRDL, the RPD is not calculated and is indicated as "NC" on Form VI.

If the duplicate sample results are outside the control limits, flag all the data for samples received associated with that duplicate sample with an "*" on Forms I and VI (Figures 3 and 4). In the instance where there is more than one duplicate sample per Case, if one duplicate result is not within contract criteria, flag all the samples of the same matrix in the Case.

13.2.6 Before samples are analyzed under the method and the CLP contract, the instrumental detection limits (in ug/L) must be determined initially and then at least quarterly (every 3 months), and must meet the levels specified in Table 2. The instrumental detection limits (in ug/L) shall be determined by multiplying by 3, the average of the standard deviations obtained on three nonconsecutive days from the analysis of a standard solution (each analyte in reagent water) at a concentration 3 to 5 times IDL, with 7 consecutive measurements per day. IDLs must be determined and reported for each wavelength used in the analysis of the samples.

For each Case, IDLs must be reported on QA Report Form VII (Figure 9). If multiple AA instruments are used for the analysis of an element with a Case, the highest IDL for the AAs must be reported for that Case.

13.2.7 Because of the nature of the furnace AA technique, the special procedures summarized in Figure 11 will be required for quantitation.

13.2.7.1 All furnace analyses, except during Full Methods of Standard Addition (MSA), will require duplicate injections for which the average absorbance or "concentration" will be reported. All analyses must fall within the calibration range. The raw data package must contain absorbance or "concentration" values for both injections, the average value and the relative standard deviation (RSD) or coefficient of variation (CV). For concentrations greater than CRDL, the duplicate injection readings must agree within 20 percent RSD or CV, or the sample must be rerun once (i.e., two additional burns). If the readings are still out, flag the value with an "M" on Form I (Figure 3).

13.2.7.2 All furnace analyses for each sample, including the laboratory control sample, will require at least a single analytical spike to determine if the MSA will be required for quantitation. An analytical spike is not required on the predigest spike sample when the predigest spike sample recovery is within the specified control limits of 75 to 125 percent or when the sample concentration is greater than 4 times the predigest spike concentration. The spike* will be required to be at a concentration (in the sample) twice the contract required detection limit (CRDL). The percent recovery of the spike, calculated by the same formula in Section 13.2.4 will then determine how the sample will be quantitated as follows.

13.2.7.2.1 If the spike recovery is less than 40 percent the sample must be diluted and rerun with another spike. Dilute the sample by a factor of 5 to 10 and rerun. This step must only be performed once. If after the dilution the spike recovery is still <40 percent, report data and flag with an "E" to indicate interference problems.

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*Spikes are postdigest spikes to be prepared prior to analysis by adding a known quantity of the analyte to an aliquot of the digested sample. The unspiked sample aliquot must be compensated for any volume change in the spike samples by addition of deionized water to the unspiked sample aliquot.

13.2.7.2.2 If the spike recovery is greater than 40 percent and the sample absorbance or concentration is <50 percent of the spike, report the sample results to the IDL. If the spike recovery is less than 85 percent or greater than 115 percent, flag the result with a "W".

13.2.7.2.3 If the sample absorbance or concentration is >50 percent of the spike and the spike recovery is between 85 percent and 115 percent, the sample should be quantitated directly from the calibration curve and report to the IDL.

13.2.7.2.4 If the sample absorbance or concentration is >50 percent of the spike and the spike recovery is less than 85 percent or greater than 115 percent, the sample must be quantitated by MSA.

13.2.7.3 The following procedures will be incorporated into MSA analyses.

13.2.7.3.1 Data from MSA calculations must be within the linear range as determined by the calibration curve generated at the beginning of the analytical run.

13.2.7.3.2 The sample and three spikes must be analyzed consecutively for MSA quantitation (the "initial" spike run data is specifically excluded from use in the MSA quantitation). Each full MSA counts as 2 "analytical samples" toward determining 10 percent QC frequency (i.e., 5 full MSAs can be performed between calibration verifications).

13.2.7.3.3 For analytical runs containing only MSAs, single injections can be used for QC samples during that run.

13.2.7.3.4 Spikes should be prepared such that:

- Spike 1 is approximately 50 percent of the sample absorbance.
- Spike 2 is approximately 100 percent of the sample absorbance.
- Spike 3 is approximately 150 percent of the sample absorbance.

13.2.7.3.5 The data for each MSA analysis should be clearly identified in the raw data documentation along with the slope, intercept and correlation coefficient (r) for the least squares fit of the data and the results reported on Form VIII (Figure 5). Reported values obtained by MSA are flagged on the data sheet (Form I) with the letter "S" (see Figure 3).

13.2.7.3.6 If the correlation coefficient (r) for a particular analysis is less than 0.995 the MSA analyses must be repeated once. If the correlation coefficient is still <0.995, report the results on Form I (Figure 3) from the run with the best "r" and flag the result with a "+".

13.2.7.4 Laboratory Control Samples (LCS) - Aqueous and solid laboratory quality control samples must be analyzed for each analyte using the same sample preparations, analytical methods and QA/QC procedures employed for the EPA samples received.

The aqueous LCS solution must be obtained from EPA (if unavailable, the EPA Initial Calibration Verification solutions may be used). The aqueous LCS must be prepared and analyzed with the aqueous samples for each of the procedures applied to each Case of samples received. One aqueous LCS must be analyzed for every 20 aqueous samples received, or for each batch of aqueous samples digested whichever is more frequent. All aqueous LCS results will be reported on Form VII (Figure 9) in terms of true concentration and percent recovery (%R) as calculated by:

%R = (Observed/True) x 100

where "observed" is the measured concentration. If the %R for the aqueous LCS falls outside the control limits of 80 percent - 120 percent, the analyses must be terminated, the problems corrected and the previous samples associated with that LCS re-analyzed (i.e., previous 19 samples or the batch of samples from the Case).

14.0 REFERENCES

1. U.S. EPA Environmental Monitoring and Support Laboratory, Cincinnati, OH, August 1977. "Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue," Revised October 1980.

2. EPA (U.S. Environmental Protection Agency). Handbook for Analytical Quality Control in Water and Wastewater Laboratories, EPA-600/4079-019.

3. EPA (U.S. Environmental Protection Agency). "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020.

4. Ibid, Methods 204.2 (Sb), 206.2 (As), 213.2 (Cd), 239.2 (Pb), 270.2 (Se), 272.2 (Ag) and 279.2 (Tl).

5. Annual Book of ASTM Standards, Part 31.

6. Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Aug. 1977. "Carcinogens - Working With Carcinogens," Publication No. 77-206.

7. Occupational Safety and Health Administration, OSHA 2206 (Revised, January 1976). "OSHA Safety and Health Standards, General Industry" (29 CFR 1910).

8. American Chemical Society Publications Committee on Chemical Safety, "Safety in Academic Chemistry Laboratories," 3rd Edition, 1979.

9. Lindahl, P. C., Argonne National Laboratory. "Furnace Atomic Absorption Spectrophotometric Method for Trace Element Analysis," modified from the Contract Laboratory Program, SOW No. 785.

Table 4. Spiking Levels for Spiked Sample Analysis[a]

Element (ug/L)	Water (ug/L)	Sediment (ug/L)
Antimony	100	60
Arsenic	40	10
Cadmium	5	5
Lead	20	5
Selenium	10	5
Silver	20	10
Thallium	50	10

a. The levels shown indicate concentrations in the final digestate of the spiked sample (200 mL final volume).

1. Add a portion of the sample to a tared weighing dish. Weigh and record the weight.

2. Place weighing dish plus sample, with the cover tipped to allow for moisture escape, in a drying oven that is set at 103° to 105°C. Perform this task in a well-ventilated area.

3. Dry the sample to constant weight. Cool the sample in a desiccator with the weighing dish cover in place before each weighing. Record each weight. Do not analyze the dried sample.

4. Calculate and report data on a dry weight basis. Also report the percent solids for each sample.

$$\text{Percent solids} = \frac{\text{Sample Dry Weight}}{\text{Sample Wet Weight}} \times 100$$

Figure 1. Determination of Percent Solids

DOE ENVIRONMENTAL SURVEY Date ______________

ATTACHMENT 2

COVER PAGE
INORGANIC ANALYSES DATA PACKAGE

Lab Name ________________________ Case No. ________________________
________________________ Q.C. Report No. ________________________

Sample Numbers

DOE No.	Lab ID No.	DOE No.	Lab ID No.

Comments: ____
____
____

Inorganic Analyses Data Package for USEPA CLP Method ________
if not indicate the method or method combinations
DOE ES ICP Method ________
DOE ES Furnace AA Method ________
DOE ES Cold Vapor AA Method ________
ICP interelement and background corrections applied? Yes ____ No ____.
If yes, corrections applied before ____ or after ____ generation of raw data.

Footnotes:

NR - Not required at this time.
Form I:
Value - If the result is a value greater than or equal to the instrument detection limit but less than the required detection limit (See DOE methods), report the value in brackets (i.e., [10]).
U - Indicates element was analyzed for but not detected. Report with the instrument detection limit value (e.g., [10U]).
E - Indicates a value estimated or not reported due to the presence of interference. Explanatory note included on cover page.
S - Indicates value determined by Method of Standard Additions.
N - Indicates spike sample recovery is not within control limits.
* - Indicates duplicate analysis is not within control limits.
+ - Indicates the correlation coefficient for method of standard additions is less than 0.995.
M - Indicates duplicate injection results exceed control limits.

Indicate method used: P for ICP; A for Flame AA; F for Furnace AA; and CV for Cold Vapor AA.

DOE - 5/87

Figure 2. Cover Page, Inorganic Analyses Data Package

Form I

DOE Sample No.

Date ____________

INORGANIC ANALYSIS DATA SHEET

Lab Name ____________
Case No. ____________
Lab Receipt Date ____________
Lab Sample ID. No. ____________
QC Report No. ____________

Elements Identified and Measured

Concentration: Low ________ Medium ________

Matrix: Water ________ Soil ________ Sludge ________ Other ________

ug/L or mg/kg dry weight (Circle One)

1. Aluminum ____________
2. Antimony ____________
3. Arsenic ____________
4. Barium ____________
5. Beryllium ____________
6. Cadmium ____________
7. Calcium ____________
8. Chromium ____________
9. Cobalt ____________
10. Copper ____________
11. Iron ____________
12. Lead ____________
13. Magnesium ____________
14. Manganese ____________
15. Mercury ____________
16. Nickel ____________
17. Potassium ____________
18. Selenium ____________
19. Silver ____________
20. Sodium ____________
21. Thallium ____________
22. Vanadium ____________
23. Zinc ____________

Percent Solids (%) ____________

Footnotes: For reporting results, standard result qualifiers are used as defined on Cover Page. Additional flags or footnotes explaining results are encouraged. Definition of such flags must be explicit and contained on Cover Page, however.

Comments: ____________

Lab Manager ____________

DOE - 5/87

Figure 3. Inorganic Analysis Data Sheet

Form VI

Q.C. Report No. ____________

DUPLICATES

Lab Name ______________________
Date ______________________

Case No. ______________________
DOE Sample No. ______________________
Lab Sample ID No. ______________________
Units ______________________

Matrix ______________

Compound	Control Limit[1]	Sample (S)	Duplicate (D)	RPD[2]
Metals:				
1. Aluminum				
2. Antimony				
3. Arsenic				
4. Barium				
5. Beryllium				
6. Cadmium				
7. Calcium				
8. Chromium				
9. Cobalt				
10. Copper				
11. Iron				
12. Lead				
13. Magnesium				
14. Manganese				
15. Mercury				
16. Nickel				
17. Potassium				
18. Selenium				
19. Silver				
20. Sodium				
21. Thallium				
22. Vanadium				
23. Zinc				
Other: ______				

*Out of Control

[1] To be added at a later date.

[2] RPD - $[|S - D|/((S + D)/2] \times 100$

NC - Non calculated RPD due to value(s) less than RDL.

DOE - 5/87

Figure 4. Duplicates

FORM VIII

Q.C. Report No. ____________

STANDARD ADDITION RESULTS

Lab Name ____________________ Case No. ____________________
Date ______________________ Units: ug/L

DOE Sample No.	Element	Matrix	0 Add Abs.	Con.	Abs.2	Con.	Abs.2	Con.	Abs.2	Con.	3r*

[1] Matrix abbreviations: Low Solid, LS; Medium Solid, MS; Low Aqueous, LA; Medium Aqueous, MA.

[2] CON is the concentration added, ABS. is the instrument readout in absorbance or concentration.

[3] Concentration as determined by MSA.

*"r" is the correlation coefficient.

+ - correlation coefficient is outside of control window of 0.995.

Figure 5. Standard Addition Results

Form II

Q.C. Report No. ________________

INITIAL AND CONTINUING CALIBRATION VERIFICATION[3]

Lab Name ________________________ Case No. ________________________

Date ____________________________ Units: ug/L

Compound	Initial Calibration			Continuing Calibration[2]					
Metals:	True Value	Found	%R	True Value	Found	%R	Found	%R	Method[4]
1. Aluminum									
2. Antimony									
3. Arsenic									
4. Barium									
5. Beryllium									
6. Cadmium									
7. Calcium									
8. Chromium									
9. Cobalt									
10. Copper									
11. Iron									
12. Lead									
. Magnesium									
14. Manganese									
15. Mercury									
16. Nickel									
17. Potassium									
18. Selenium									
19. Silver									
20. Sodium									
21. Thallium									
22. Vanadium									
23 Zinc									
Other: ________									

[1] Initial Calibration Source ____________

[2] Continuing Calibration Source __________

[3] Control Limits: Mercury and Tin 80-120; Other Metals 90-110; Cyanide 85-115

[4] Indicate Analytical Method Used: P - ICP; A - Flame AA; F - Furnace AA;
CV - Cold Vapor AA

DOE - 5/87

Figure 6. Initial and Continuing Calibration Verification

Form III

Q.C. Report No. ________________

BLANKS

Lab Name ________________________ Case No. ________________

Date ________________________ Units ________________

Compound	Initial Calibration Blank Value	Continuing Calibration Blank Value 1	2	3	4	Preparation Blank Matrix: 1	Matrix: 2
Metals:							
1. Aluminum							
2. Antimony							
3. Arsenic							
4. Barium							
5. Beryllium							
6. Cadmium							
7. Calcium							
8. Chromium							
9. Cobalt							
10. Copper							
11. Iron							
12. Lead							
13. Magnesium							
14. Manganese							
15. Mercury							
16. Nickel							
17. Potassium							
18. Selenium							
19. Silver							
20. Sodium							
21. Thallium							
22. Vanadium							
23. Zinc							
Other: ________							

[1] Reporting Units: aqueous, ug/L; solid mg/kg

DOE - 5/87

Figure 7. Blanks

Form V

Q.C. Report No. ____________

SPIKE SAMPLE RECOVERY

Lab Name ________________________
Date ________________________

Case No. ________________________
DOE Sample No. ________________________
Lab Sample ID No. ________________________
Units ________________________

Matrix ______________

Compound	Control Limit %R	Spiked Sample Result (SSR)	Sample Result (SR)	Spiked Added (SA)	%R[1]
Metals:					
1. Aluminum	75-125				
2. Antimony	"				
3. Arsenic	"				
4. Barium	"				
5. Beryllium	"				
6. Cadmium	"				
7. Calcium	"				
8. Chromium	"				
9. Cobalt	"				
[illegible] Copper	"				
11. Iron	"				
12. Lead	"				
13. Magnesium	"				
14. Manganese	"				
15. Mercury	"				
16. Nickel	"				
17. Potassium	"				
18. Selenium	"				
19. Silver	"				
20. Sodium	"				
21. Thallium	"				
22. Vanadium	"				
23. Zinc	"				
Other: ________					

[1] %R = [(SSR - SR)/SA] x 100
"N" - Out of control
"NR" - Not required
Comments: ____

DOE - 5/87

Figure 8. Spike Sample Recovery

Form VII

Q.C. Report No. ________________

INSTRUMENT DETECTION LIMITS AND LABORATORY CONTROL SAMPLE

Lab Name ________________________ Case No. ________________________
Date ________________________ LCS No. ________________________

Compound	Required Detection Limits (CRDL)-ug/1 ICP/AA	Required Detection Limits (CRDL)-ug/1 Furnace/CV	Instrument Detection Limits (IDL)-ug/1 ICP/AA ID#____	Instrument Detection Limits (IDL)-ug/1 Furnace ID#____	Lab Control Sample ug/L mg/kg (circle one) True	Found	%R
Metals:							
1. Aluminum	200	--					
2. Antimony	150	60					
3. Arsenic	250	10					
4. Barium	200	--					
5. Beryllium	5	--					
6. Cadmium	20	5					
7. Calcium	5000	--					
8. Chromium	10	--					
9. Cobalt	50	--					
10. Copper	25	--					
11. Iron	100	--					
12. Lead	200	5					
13. Magnesium	5000	--					
14. Manganese	15	--					
15. Mercury	--	0.2					
16. Nickel	40	--					
17. Potassium	5000	--					
18. Selenium	400	5					
19. Silver	30	10					
20. Sodium	5000	--					
21. Thallium	200	10					
22. Vanadium	50	--					
23. Zinc	20	--					
Other: ________							

NR - Not required

DOE - 5/87

Figure 9. Instrument Detection Limits and Laboratory Control Sample

FORM XIa (Quarterly)

INSTRUMENT DETECTION LIMITS - ICP/aa

Lab Name ____________________
ICP/Flame AA (Circle One)
Model Number ____________________

Element	Wave-length (nm)	CRDL (ug/L)	IDL (ug/L)	Element	Wave-length (nm)	CRDL (ug/L)	IDL (ug/L)
1. Aluminum				13. Magnesium			
2. Antimony				14. Manganese			
3. Arsenic				15. Mercury			
4. Barium				16. Nickel			
5. Beryllium				17. Potassium			
6. Cadmium				18. Selenium			
7. Calcium				19. Silver			
8. Chromium				20. Sodium			
9. Cobalt				21. Thallium			
10. Copper				22. Vanadium			
11. Iron				23. Zinc			
12. Lead							

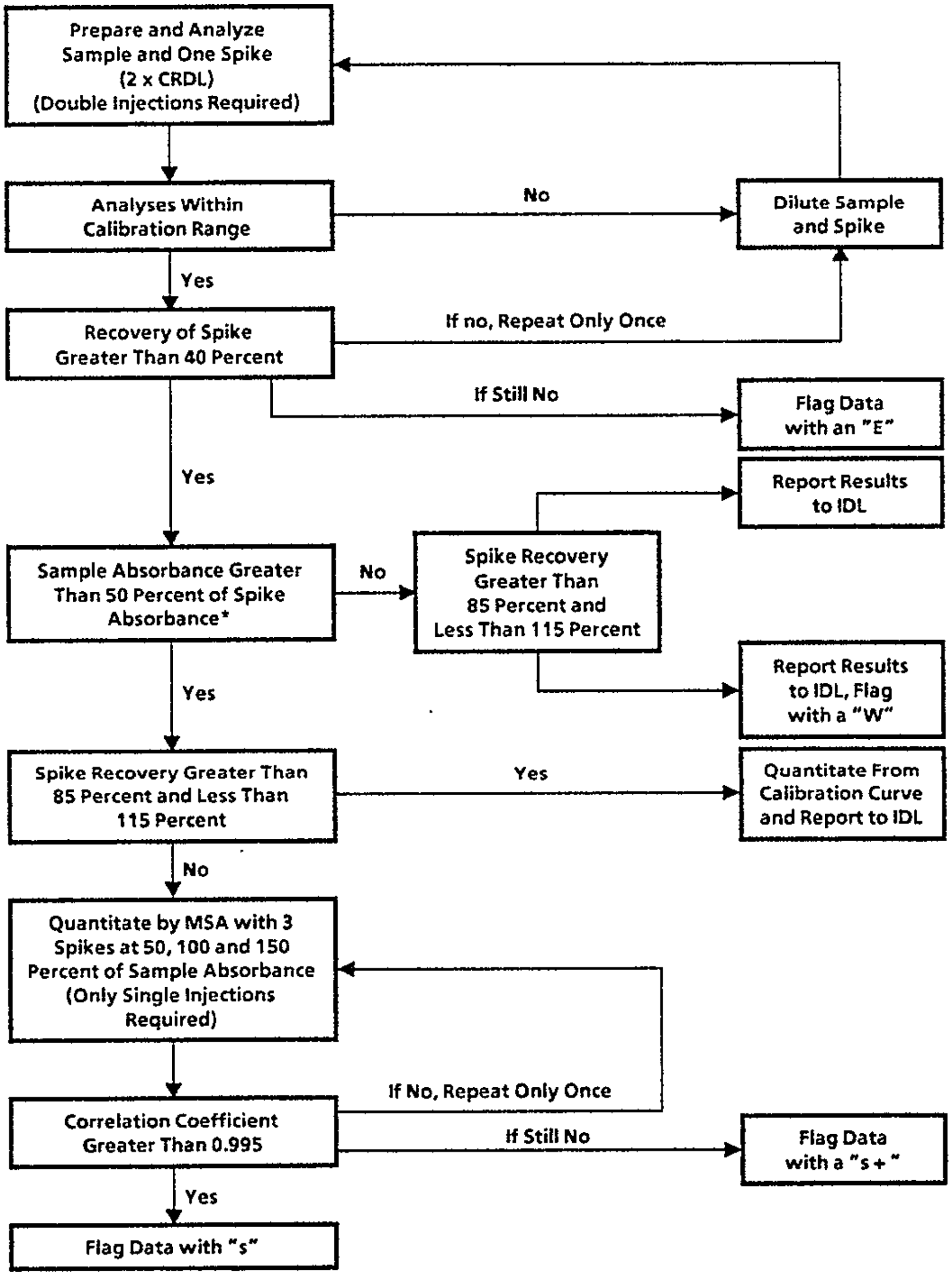
Footnotes:
- Indicate the instrument for which the IDL applies with a "P" (for ICP), an "A" (for Flame AA), an "F" (for Furnace AA), or a "CV" (for Cold Vapor AA) behind the IDL value.
- Indicate elements commonly run with background correction (AA) with a "B" behind the analytical wavelength.
- If more than one ICP/Flame or Furnace AA is used, submit separate Forms XI-XIII for each instrument.

Comments: ____
____
____

Lab Manager ____________________

DOE 5/87

Figure 10. Instrument Detection Limits — ICP/AA


Prepare and Analyze Sample and One Spike (2 x CRDL) (Double Injections Required)
Analyses Within Calibration Range
No
Dilute Sample and Spike
Yes
Recovery of Spike Greater Than 40 Percent
If no, Repeat Only Once
If Still No
Flag Data with an "E"
Yes
Report Results to IDL
Sample Absorbance Greater Than 50 Percent of Spike Absorbance*
No
Spike Recovery Greater Than 85 Percent and Less Than 115 Percent
Report Results to IDL, Flag with a "W"
Yes
Spike Recovery Greater Than 85 Percent and Less Than 115 Percent
Yes
Quantitate From Calibration Curve and Report to IDL
No
Quantitate by MSA with 3 Spikes at 50, 100 and 150 Percent of Sample Absorbance (Only Single Injections Required)
If No, Repeat Only Once
Correlation Coefficient Greater Than 0.995
If Still No
Flag Data with a "s+"
Yes
Flag Data with "s"

*Spike absorbance defined as (absorbance of spike sample) minus (absorbance of the sample).

Figure 11. Furnace Atomic Absorption Analysis Scheme

MERCURY IN WATER BY MANUAL COLD VAPOR AA
(Method 245.1 CLP-M*)

1.0 SCOPE AND APPLICATION

1.1 In addition to inorganic forms of mercury, organic mercurials may also be present. These organo-mercury compounds will not respond to the cold vapor atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds, but recent studies have shown that a number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potassium persulfate has been found to give approximately 100 percent recovery when used as the oxidant with these compounds. Therefore, a persulfate oxidation step following the addition of the permanganate has been included to ensure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement. A heat step is required for methyl mercuric chloride when present in or spiked into a natural system.

1.2 The range of the method may be varied through instrument and/or recorder expansion. Using a 100-mL sample, a detection limit of 0.2 ug Hg/L can be achieved.

1.3 If additional sensitivity is required, a 200-mL sample with recorder expansion may be used provided the instrument does not produce undue noise. Using a Coleman MAS-50 with a drying tube of magnesium perchlorate and a variable recorder, 2 mv was set to read full scale. With these conditions, and distilled water solutions of mercuric chloride at concentrations of 0.15, 0.10, 0.05 and 0.025 ug/L the standard deviations were ±0.027, ±0.0006, ±0.01 and ±0.004. Percent recoveries at these levels were 107, 83, 84, and 96 percent, respectively.

---

*CLP-M modified for the Contract Laboratory Program

2.0 SUMMARY OF METHOD

2.1 The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. Organic mercury compounds are oxidized and the mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration and recorded in the usual manner.

3.0 INTERFERENCES

3.1 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from distilled water.

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

3.3 Sea water, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 mL). During the oxidation step, chlorides are converted to free chlorine which will also absorb radiation of 253 nm. Care must be taken to assure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the BOD bottle must be purged before the addition of stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from sea water using this technique.

3.4 Interference from certain volatile organic materials which will absorb at this wavelength is also possible. A preliminary run without reagents should determine if this type of interference is present. A simple correction that may be used: if an interference has been found to be present, the sample should be analyzed both by using the regular procedure and again under oxidizing conditions only, that is without the reducing reagents. The true mercury value can then be obtained by subtracting the two values.

4.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

4.1 Until more conclusive data are obtained, samples should be preserved by acidification with nitric acid to a pH of 2 or lower immediately at the time of collection.

5.0 SAFETY

5.1 Directions for the disposal of mercury-containing wastes are given in the Annual ASTM Book of Standards, Part 31, "Water," p. 349, Method D3223 (1976).

6.0 APPARATUS AND EQUIPMENT

6.1 Atomic absorption spectrophotometer - (See Note 1) Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

Note 1: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

6.2 Mercury hollow cathode lamp - Westinghouse WL-22847, argon filled, or equivalent.

6.3 Recorder - Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

6.4 Absorption cell - Standard spectrophotometer cells 10-cm long, having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing, 1-in. O.D. x 4-1/2-in. The ends are ground perpendicular to the longitudinal axis and quartz windows (1-in. diameter x 1/16-in. thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2-in. by 2-in. cards. One inch diameter holes are cut in the middle of each card; the cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to find the maximum transmittance.

6.5 Air pump - Any peristaltic pump capable of delivering air at 1 L/min may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

6.6 Flowmeter - Capable of measuring an air flow of 1 L/min.

6.7 Aeration tubing - A straight glass frit having a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

6.8 Drying tube - 6-in. x 3/4-in. diameter tube containing 20 g of magnesium perchlorate (see Note 2). The apparatus is assembled as shown in Figure 1.

Note 2: In place of the magnesium perchlorate drying tube, a small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

7.0 REAGENTS

7.1 Sulfuric acid - Concentrated, reagent grade.

7.1.1 Sulfuric acid (0.5 N) - Dilute 14.0 mL of concentrated sulfuric acid to 1.0 L.

7.2 Nitric acid - Concentrated reagent grade of low mercury content (see Note 3).

Note 3: If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

7.3 Stannous sulfate solution - Add 25 g of stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)

7.4 Sodium chloride-hyroxylamine sulfate solution - Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in distilled water and dilute to 100 mL. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

7.5 Potassium permanganate solution (5 percent) - Dissolve 5 g of potassium permanganate in 100 mL of distilled water.

7.6 Potassium persulfate solution (5 percent) - Dissolve 5 g of potassium persulfate in 100 mL of distilled water.

7.7 Mercury stock solution (1 mL = 1 mg Hg) - Dissolve 0.1354 g of mercuric chloride in 75 mL of distilled water. Add 10 mL of concentrated nitric acid and adjust the volume to 100.0 mL.

7.8 Mercury working solution - Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 ug/mL. This working standard and the dilutions of the mercury stock solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15 percent nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

8.0 CALIBRATION

8.1 Transfer 0-, 0.5-, 1.0-, 2.0-, 5.0- and 10.0-mL aliquots of the mercury working solution containing 0 to 1.0 ug of mercury to a series of 300-mL BOD bottles. Add enough distilled water to each bottle to make a total volume of 100 mL. Mix thoroughly and add 5 mL of concentrated sulfuric acid and 2.5 mL of concentrated nitric acid to each bottle. Add 15 mL of potassium permanganate solution to each bottle and allow to stand at least 15 min. Add 8 mL of potassium persulfate solution to each bottle and heat for 2 h in a water bath maintained at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. When the solution has been decolorized, wait 30 s, add 5 mL of the stannous sulfate solution and immediately attach the bottle to the aeration apparatus forming a closed system.

8.2 At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 L/min, is allowed to run continuously (see Note 4). The absorbance will increase and reach maximum within 30 s. As soon as the recorder pen levels off, approximately 1 min, open the bypass valve and continue the aeration until the absorbance returns to its minimum value (see Note 5). Close the bypass valve, remove the stopper and frit from the BOD bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting peak height versus micrograms of mercury.

Note 4: An open system where the mercury vapor is passed through the absorption cell only once may be used instead of the closed system.

Note 5: Because of the toxic nature of mercury vapor, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as:

1. Equal volumes of 0.1 M $KMnO_4$, and 10 percent H_2SO_4
2. 0.25 percent iodine in a 3 percent KI solution

Specially treated charcoal that will adsorb mercury vapor is also available from Barnebey and Cheney, E. 8th Ave. and N. Cassidy St., Columbus, Ohio 43219, Cat 80-13 or 80-22.

9.0 PROCEDURE

9.1 Transfer 100 mL, or an aliquot diluted to 100 mL, containing not more than 1.0 ug of mercury, to a 300-mL BOD bottle. Add 5 mL of sulfuric acid and 2.5 mL of concentrated nitric acid mixing after each addition. Add 15 mL of potassium permanganate solution to each sample bottle (see Note 6). For sewage samples additional permanganate may be required. Shake and add additional portions of potassium permanganate solution, if necessary until the purple color persists for at least 15 min. Add 8 mL of potassium persulfate solution to each bottle and heat for 2 h in a water bath at 95°C.

Note 6: The same amount of potassium permanganate solution added to the samples should be present in standards and blanks.

9.2 Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate (see Note 7). After a delay of at least 30 s add 5 mL of stannous sulfate solution and immediately attach the bottle to the aeration apparatus. Continue as described under Section 8.2.

Note 7: Add reductant in 6-mL increments until potassium permanganate is completely reduced.

10.0 CALCULATION

10.1 Determine the peak height of the unknown from the chart and read the mercury value from the standard curve.

10.2 Calculate the mercury concentration in the sample by the following equation.

$$\text{Concentration (ug Hg/L)} = A \times \frac{1000}{V}$$

where:

A = Amount of Hg in aliquot (ug)

V = Volume of aliquot (mL).

11.0 REPORTING

11.1 Report mercury concentrations as follows - Below 0.2 ug/L, 0.2U; between 0.2 and 10 ug/L, one decimal; above 10 ug/L, whole numbers.

11.2 All data should be recorded on Forms I, II, III, V, VI, VII, X, and XIb (Figures 2-9).

12.0 REFERENCES

1. Kopp, J. F., M. C. Longbottom, and L. B. Lobring, Jan. 1972. "Cold Vapor Method for Determining Mercury," AWWA, Vol. 64, p. 20.
2. Annual Book of ASTM Standards, Part 31, "Water," Standard D3223-73, p. 343 (1976).
3. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p. 156 (1975).

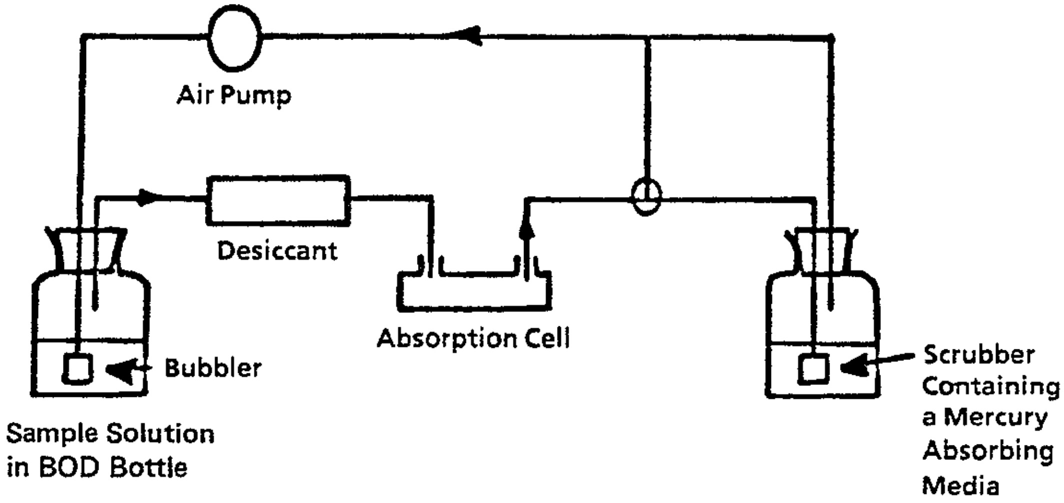

Air Pump
Desiccant
Absorption Cell
Bubbler
Sample Solution
in BOD Bottle
Scrubber
Containing
a Mercury
Absorbing
Media

Figure 1. Apparatus for Flameless Mercury Determination

DOE ENVIRONMENTAL SURVEY Date ____________

COVER PAGE
INORGANIC ANALYSES DATA PACKAGE

Lab Name ____________ Case No. ____________

____________ Q.C. Report No. ____________

Sample Numbers

DOE No.	Lab ID No.	DOE No.	Lab ID No.

Comments: ____________

Inorganic Analyses Data Package for USEPA CLP Method ______
if not indicate the method or method combinations
DOE ES ICP Method ______
DOE ES Furnace AA Method ______
DOE ES Cold Vapor AA Method ______
ICP interelement and background corrections applied? Yes ____ No ____.
If yes, corrections applied before ____ or after ____ generation of raw data.

Footnotes:

NR - Not required at this time.
Form I:
Value - If the result is a value greater than or equal to the instrument detection limit but less than the required detection limit (See DOE methods), report the value in brackets (i.e., [10]).
U - Indicates element was analyzed for but not detected. Report with the instrument detection limit value (e.g., [10U]).
E - Indicates a value estimated or not reported due to the presence of interference. Explanatory note included on cover page.
S - Indicates value determined by Method of Standard Additions.
N - Indicates spike sample recovery is not within control limits.
* - Indicates duplicate analysis is not within control limits.
+ - Indicates the correlation coefficient for method of standard additions is less than 0.995.
M - Indicates duplicate injection results exceed control limits.

Indicate method used: P for ICP; A for Flame AA; F for Furnace AA; and CV for Cold Vapor AA.

DOE - 5/87

92124571050

Form I

DOE Sample No.

Date ____________

INORGANIC ANALYSIS DATA SHEET

Lab Name ____________________ Case No. ____________________

Lab Receipt Date ____________________

Lab Sample ID. No. ____________ QC Report No. ____________________

Elements Identified and Measured

Concentration: Low ________ Medium ________

Matrix: Water ________ Soil ________ Sludge ________ Other ________

ug/L or mg/kg dry weight (Circle One)

1. Aluminum ____________
2. Antimony ____________
3. Arsenic ____________
4. Barium ____________
5. Beryllium ____________
6. Cadmium ____________
7. Calcium ____________
8. Chromium ____________
9. Cobalt ____________
10. Copper ____________
11. Iron ____________
12. Lead ____________
13. Magnesium ____________
14. Manganese ____________
15. Mercury ____________
16. Nickel ____________
17. Potassium ____________
18. Selenium ____________
19. Silver ____________
20. Sodium ____________
21. Thallium ____________
22. Vanadium ____________
23. Zinc ____________

Percent Solids (%) ____________

Footnotes: For reporting results, standard result qualifiers are used as defined on Cover Page. Additional flags or footnotes explaining results are encouraged. Definition of such flags must be explicit and contained on Cover Page, however.

Comments: ____

Lab Manager ____________________

DOE - 5/87

Figure 2. Inorganic Analysis Data Sheet

Form II

Q.C. Report No. ____________

INITIAL AND CONTINUING CALIBRATION VERIFICATION[3]

Lab Name ____________________ Case No. ____________________

Date ____________________ Units: ug/L

Compound	Initial Calibration			Continuing Calibration[2]					
Metals:	True Value	Found	%R	True Value	Found	%R	Found	%R	Method[4]
1. Aluminum									
2. Antimony									
3. Arsenic									
4. Barium									
5. Beryllium									
6. Cadmium									
7. Calcium									
8. Chromium									
9. Cobalt									
10. Copper									
11. Iron									
12. Lead									
13. Magnesium									
14. Manganese									
15. Mercury									
16. Nickel									
17. Potassium									
18. Selenium									
19. Silver									
20. Sodium									
21. Thallium									
22. Vanadium									
23 Zinc									
Other: ______									

[1] Initial Calibration Source ____________

[2] Continuing Calibration Source ____________

[3] Control Limits: Mercury and Tin 80-120; Other Metals 90-110; Cyanide 85-115

[4] Indicate Analytical Method Used: P - ICP; A - Flame AA; F - Furnace AA;
CV - Cold Vapor AA

DOE - 5/87

Figure 3. Initial and Continuing Calibration Verification

Form III

Q.C. Report No. ________________

BLANKS

Lab Name ________________ Case No. ________________
Date ________________ Units ________________

Compound	Initial Calibration Blank Value	Continuing Calibration Blank Value				Preparation Blank	
		1	2	3	4	Matrix: 1	Matrix: 2
Metals:							
1. Aluminum							
2. Antimony							
3. Arsenic							
4. Barium							
5. Beryllium							
6. Cadmium							
7. Calcium							
8. Chromium							
9. Cobalt							
10. Copper							
11. Iron							
12. Lead							
13. Magnesium							
14. Manganese							
15. Mercury							
16. Nickel							
17. Potassium							
18. Selenium							
19. Silver							
20. Sodium							
21. Thallium							
22. Vanadium							
23. Zinc							
Other: ________							

---

[1] Reporting Units: aqueous, ug/L; solid mg/kg

DOE - 5/87

Figure 4. Blanks

Form V

Q.C. Report No. ____________

SPIKE SAMPLE RECOVERY

Lab Name ______________________
Date ______________________

Case No. ______________________
DOE Sample No. ______________________
Lab Sample ID No. ______________________
Units ______________________

Matrix ______________

Compound	Control Limit %R	Spiked Sample Result (SSR)	Sample Result (SR)	Spiked Added (SA)	%R[1]
Metals:					
1. Aluminum	75-125				
2. Antimony	"				
3. Arsenic	"				
4. Barium	"				
5. Beryllium	"				
6. Cadmium	"				
7. Calcium	"				
8. Chromium	"				
9. Cobalt	"				
10. Copper	"				
11. Iron	"				
12. Lead	"				
13. Magnesium	"				
14. Manganese	"				
15. Mercury	"				
16. Nickel	"				
17. Potassium	"				
18. Selenium	"				
19. Silver	"				
20. Sodium	"				
21. Thallium	"				
22. Vanadium	"				
23. Zinc	"				
Other: ______					

[1] %R = [(SSR - SR)/SA] x 100
"N" - Out of control
"NR" - Not required
Comments: ______________________________

DOE - 5/87

Figure 5. Spike Sample Recovery

92124571054

Form VI

Q.C. Report No. ____________

DUPLICATES

Lab Name ____________________________
Date ____________________________

Case No. ____________________________
DOE Sample No. ______________________
Lab Sample ID No. ___________________
Units ____________________________

Matrix ______________

Compound	Control Limit[1]	Sample (S)	Duplicate (D)	RPD[2]
Metals:				
1. Aluminum				
2. Antimony				
3. Arsenic				
4. Barium				
5. Beryllium				
6. Cadmium				
7. Calcium				
8. Chromium				
9. Cobalt				
10. Copper				
11. Iron				
12. Lead				
13. Magnesium				
14. Manganese				
15. Mercury				
16. Nickel				
17. Potassium				
18. Selenium				
19. Silver				
20. Sodium				
21. Thallium				
22. Vanadium				
23. Zinc				
Other: ______				

*Out of Control

[1] To be added at a later date.

[2] RPD - [|S - D|/((S + D)/2] x 100

NC - Non calculated RPD due to value(s) less than RDL.

DOE - 5/87

Figure 6. Duplicates

Form VII

Q.C. Report No. ________________

INSTRUMENT DETECTION LIMITS AND LABORATORY CONTROL SAMPLE

Lab Name ____________________ Case No. ____________________
Date ____________________ LCS No. ____________________

Compound	Required Detection Limits (CRDL)-ug/1		Instrument Detection Limits (IDL)-ug/1		Lab Control Sample ug/L mg/kg (circle one)		
	ICP/AA	Furnace/CV	ICP/AA ID#____	Furnace ID#____	True	Found	%R
Metals:							
1. Aluminum	200	--					
2. Antimony	150	60					
3. Arsenic	250	10					
4. Barium	200	--					
5. Beryllium	5	--					
6. Cadmium	20	5					
7. Calcium	5000	--					
8. Chromium	10	--					
9. Cobalt	50	--					
10. Copper	25	--					
11. Iron	100	--					
12. Lead	200	5					
13. Magnesium	5000	--					
14. Manganese	15	--					
15. Mercury	--	0.2					
16. Nickel	40	--					
17. Potassium	5000	--					
18. Selenium	400	5					
19. Silver	30	10					
20. Sodium	5000	--					
21. Thallium	200	10					
22. Vanadium	50	--					
23. Zinc	20	--					
Other: ________							

NR - Not required

DOE - 5/87

Figure 7. Instrument Detection Limits and Laboratory Control Sample

FORM X

Q.C. Report No. ________________

HOLDING TIMES

Lab Name ________________________ Case No. ______________________
Date ____________________________

DOE Sample No.	Matrix	Date Received	Mercury Prep Date	Mercury Holding Time[1] (Days)	CN Prep Date	CN Holding Time[1] (Days)

[1] Holding time is defined as number of days between the date received and the sample preparation date.

DOE - 5/87

Figure 8. Holding Times

Form XIb (Quarterly)

INSTRUMENT DETECTION LIMITS - Furnace/Cold Vapor AA

Lab Name ____________________ Date ____________________

Furnace/Cold

Vapor AA Model Numbers ____________

Element	Wave-length (nm)	RDL (ug/L)	IDL (ug/L)	Element	Wave-length (nm)	RDL (ug/L)	IDL (ug/L)
1. Aluminum		NR		13. Magnesium		NR	
2. Antimony		60		14. Manganese		NR	
3. Arsenic		10		15. Mercury		0.2	
4. Barium		NR		16. Nickel		NR	
5. Beryllium		NR		17. Potassium		NR	
6. Cadmium		5		18. Selenium		5	
7. Calcium		NR		19. Silver		10	
8. Chromium		NR		20. Sodium		NR	
9. Cobalt		NR		21. Thallium		10	
10. Copper		NR		22. Vanadium		NR	
11. Iron		NR		23. Zinc		NR	
12. Lead		5					

Footnotes:
- Indicate the instrument for which the IDL applies with a "P" (for ICP), an "A" (for Flame AA), an "F" (for Furnace AA), or a "CV" (for Cold Vapor AA) behind the IDL value.
- Indicate elements commonly run with background correction (AA) with a "B" behind the analytical wavelength.
- If more than one ICP/Flame or Furnace AA is used, submit separate Forms XI-XIII for each instrument.

Comments: ____

Lab Manager ____________________

DOE 5/87

Figure 9. Instrument Detection Limits — Furnace/Cold Vapor AA

MERCURY IN SEDIMENTS BY MANUAL COLD VAPOR AA

(Method 245.5 CLP-M*)

1.0 SCOPE AND APPLICATION

1.1 This procedure measures total mercury (organic and inorganic) in soils, sediments, bottom deposits and sludge type materials.

1.2 The range of the method is 0.2 to 5 ug/g. The range may be extended above or below the normal range by increasing or decreasing sample size or through instrument and recorder control.

2.0 SUMMARY OF METHOD

2.1 A weighed portion of the sample is digested in aqua regia for 2 min at 95°C, followed by oxidation with potassium permanganate and potassium persulfate. Mercury in the digested sample is then measured by the conventional cold vapor technique.

2.2 An alternate digestion involving the use of an autoclave is described.

3.0 INTERFERENCES

3.1 The same types of interferences that may occur in water samples are also possible with sediments; i.e., sulfides, high copper, high chlorides, etc.

3.2 Volatile materials which absorb at 253.7 nm will cause a positive interference. To remove any interfering volatile materials, purge the dead air space in the BOD bottle before the addition of stannous sulfate.

---

*CLP-M modified for the Contract Laboratory Program

3.3 Sample containing high concentrations of oxidizable organic materials, as evidenced by high chemical oxygen demand values, may not be completely oxidized by this procedure. When this occurs, the recovery of organic mercury will be low. The problem can be eliminated by reducing the weight of the original sample or by increasing the amount of potassium persulfate (and consequently stannous chloride) used in the digestion.

4.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

4.1 Because of the extreme sensitivity of the analytical procedure and the omnipresence of mercury, care must be taken to avoid extraneous contamination. Sampling devices and sample containers should be ascertained to be free of mercury; the sample should not be exposed to any condition in the laboratory that may result in contact or air-borne mercury contamination.

4.2 Refrigerate solid samples upon receipt.

4.3 The sample should be analyzed without drying. A separate percent solids determination is required.

5.0 SAFETY

5.1 Directions for the disposal of mercury-containing wastes are given in the Annual ASTM Book of Standards, Part 31, "Water," p. 349, Method D3223 (1976).

6.0 APPARATUS AND EQUIPMENT

6.1 Atomic absorption spectrophotometer (See Note 1) - Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

Note 1: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

6.2 Mercury hollow cathode lamp - Westinghouse WL-22847, argon filled, or equivalent.

6.3 Recorder - Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

6.4 Absorption cell - Standard spectrophotometer cells 10-cm long, having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing, 1-in. O.D. x 4-1/2-in. The ends are ground perpendicular to the longitudinal axis and quartz windows (1-in. diameter x 1/16-in. thickness) are cemented in place. Gas inlet and outlet ports (also of plexiglass but 1/4-in. O.D.) are attached approximately 1/2 in. from each end. The cell is strapped to a burner for support and aligned in the light beam to give the maximum transmittance.

Note 2: Two 2-in. x 2-in. cards with 1-in. diameter holes may be placed over each end of the cell to assist in positioning the cell for maximum transmittance.

6.5 Air pump - Any peristaltic pump capable of delivering air at 1 L/min may be used. A Masterflex pump with electronic speed control has been found to be satisfactory. (Regulated compressed air can be used in an open one-pass system.)

6.6 Flowmeter - Capable of measuring an air flow of 1 L/min.

6.7 Aeration tubing - Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return. Straight glass tubing terminating in a coarse porous frit is used for sparging air into the sample.

6.8 Drying tube - 6 in. x 3/4 in. diameter tube containing 20 g of magnesium perchlorate (see Note 3). The apparatus is assembled as shown in Figure 1.

Note 3: In place of the magnesium perchlorate drying tube, a small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

7.0 REAGENTS

7.1 Sulfuric acid - Concentrated reagent grade of low mercury content.

7.2 Nitric acid - Concentrated reagent grade of low mercury content.

7.3 Stannous sulfate solution - Add 25 g of stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)

7.4 Sodium chloride-hydroxylamine sulfate solution - Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in distilled water and dilute to 100 mL. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

7.5 Potassium permanganate solution (5 percent) - Dissolve 5 g of potassium permanganate in 100 mL of distilled water.

7.6 Potassium persulfate solution (5 percent) - Dissolve 5 g of potassium persulfate in 100 mL of distilled water.

7.7 Mercury stock solution (1.0 mL = 1.0 mg Hg) - Dissolve 0.1354 g of mercuric chloride in 75 mL of distilled water. Add 10 mL of concentrated nitric acid and adjust the volume to 100.0 mL.

7.8 Mercury working solution - Make successive dilutions of the mercury stock solution to obtain a working standard containing 0.1 ug/mL. This working standard and the dilution of the mercury stock solutions should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15 percent nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

8.0 CALIBRATION

8.1 Transfer 0-, 0.5-, 1.0-, 2.0-, 5.0- and 10-mL aliquots of the mercury working solutions containing 0 to 1.0 ug of mercury to a series of 300-mL BOD bottles. Add enough distilled water to each bottle to make a total volume of 10 mL. Add 5 mL of concentrated sulfuric acid and 2.5 mL of concentrated nitric acid and heat 2 min in a water bath at 95°C. Allow the sample to cool and add 50 mL of distilled water, 15 mL of potassium permanganate solution and 8 mL of potassium persulfate solution to each bottle and return to the water bath for 30 min. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Add 50 mL of distilled water. Treating each bottle individually, add 5 mL of stannous sulfate solution and immediately attach the bottle to the aeration apparatus.

8.2 At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 L/min, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 s. As soon as the recorder pen levels off, approximately 1 min, open the bypass valve and continue the aeration until the absorbance returns to its minimum value (see Note 4). Close the bypass valve, remove the fritted tubing from the BOD bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting peak height versus micrograms of mercury.

Note 4: Because of the toxic nature of mercury vapor, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as:

1. Equal volumes of 0.1 N $KMnO_4$ and 10 percent H_2SO_4

2. 0.25% iodine in a 3 percent KI solution

Specially treated charcoal that will absorb mercury vapor is also available from Barnebey and Cheney, E. 8th Avenue and N. Cassidy Street, Columbus, Ohio 43219.

9.0 PROCEDURE

9.1 Weigh a representative 0.2-g portion of wet sample and place in the bottom of a BOD bottle. Add 5 mL of sulfuric acid and 2.5 mL of concentrated nitric acid mixing after each addition. Heat 2 min in a water bath at 95°C. Cool, add 50 mL of distilled water, 15 mL of potassium permanganate solution and 8 mL of potassium persulfate solution to each sample bottle. Mix thoroughly and place in the water bath for 30 min at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Add 55 mL of distilled water. Treating each bottle individually, add 5 mL of stannous sulfate solution and immediately attach the bottle to the aeration apparatus. Continue as described under Section 8.2.

9.2 An alternate digestion procedure employing an autoclave may also be used. In this method, 5 mL of concentrated sulfuric acid and 2 mL of concentrated nitric acid are added to the 0.2 g of sample. Next, 5 mL of potassium permanganate solution and 8 mL of potassium persulfate solution are added and the bottle is covered with a piece of aluminum foil. The sample is autoclaved at 121°C and 15 lbs. for 15 min. Cool, make up to a volume of 100 mL with distilled water and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Purge the dead air space and continue as described under Section 8.1.

10.0 CALCULATIONS

10.1 Measure the peak height of the unknown from the chart and read the mercury value from the standard curve.

10.2 Calculate the mercury concentration in the sample by the following equation.

$$\text{Concentration (ug Hg/g)} = \frac{A}{W}$$

where:

A = Amount of Hg in aliquot (ug)

W = Weight of aliquot (g).

11.0 REPORTING

11.1 Report mercury concentrations as follows: below 0.1 ug/g, 0.1U; between 0.1 and 1 ug/g, to the nearest 0.01 ug; between 1 and 10 ug/g, to nearest 0.1 ug; and, above 10 ug/g, to nearest ug.

11.2 All data should be recorded on Forms I, II, III, V, VI, VII, X, and XIb (Figures 2-9).

12.0 REFERENCES

1. Bishop, J. N.; 1971. "Mercury in Sediments," Ontario Water Resources Comm., Toronto, Ontario, Canada.

2. Salma, M., private communication, EPA Cal/Nev. Basin Office, Alameda, California.

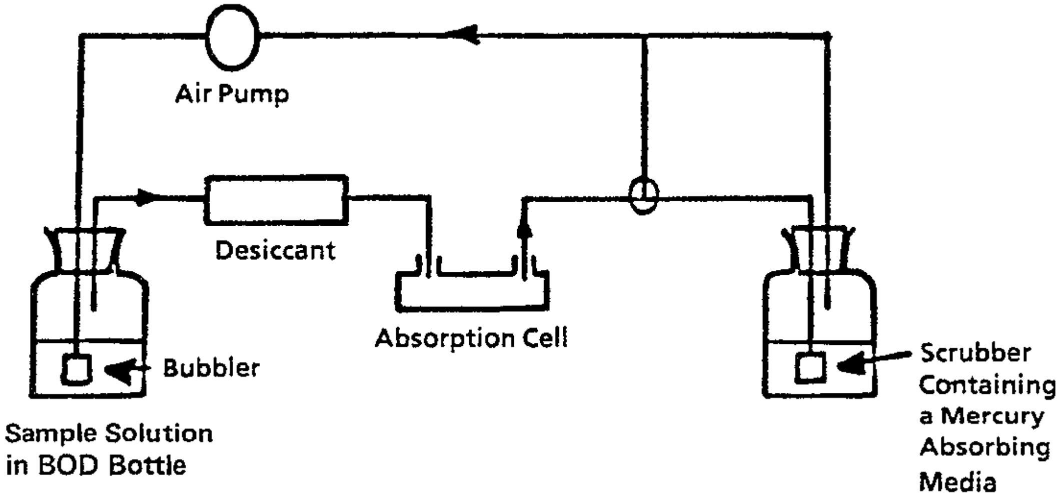

Air Pump
Desiccant
Absorption Cell
Bubbler
Sample Solution in BOD Bottle
Scrubber Containing a Mercury Absorbing Media

Figure 1. Apparatus for Flameless Mercury Determination

E ENVIRONMENTAL SURVEY Date ______________

COVER PAGE
INORGANIC ANALYSES DATA PACKAGE

Lab Name ______________________ Case No. ______________________

______________________ Q.C. Report No. ______________________

Sample Numbers

DOE No.	Lab ID No.	DOE No.	Lab ID No.

Comments: ____

____

rganic Analyses Data Package for USEPA CLP Method ________
if not indicate the method or method combinations
DOE ES ICP Method ________
DOE ES Furnace AA Method ________
DOE ES Cold Vapor AA Method ________
ICP interelement and background corrections applied? Yes ____ No ____.
If yes, corrections applied before ____ or after ____ generation of raw data.

Footnotes:
NR - Not required at this time.
Form I:
Value - If the result is a value greater than or equal to the instrument detection limit but less than the required detection limit (See DOE methods), report the value in brackets (i.e., [10]).
U - Indicates element was analyzed for but not detected. Report with the instrument detection limit value (e.g., [10U]).
E - Indicates a value estimated or not reported due to the presence of interference. Explanatory note included on cover page.
S - Indicates value determined by Method of Standard Additions.
N - Indicates spike sample recovery is not within control limits.
* - Indicates duplicate analysis is not within control limits.
+ - Indicates the correlation coefficient for method of standard additions is less than 0.995.
M - Indicates duplicate injection results exceed control limits.

icate method used: P for ICP; A for Flame AA; F for Furnace AA; and CV for Cold Vapor AA.

DOE - 5/87

Form I

DOE Sample No.

Date ____________

INORGANIC ANALYSIS DATA SHEET

Lab Name ____________________
____
Lab Sample ID. No. ____________
Case No. ____________________
Lab Receipt Date ____________
QC Report No. ______________

Elements Identified and Measured

Concentration: Low ______ Medium ______

Matrix: Water ______ Soil ______ Sludge ______ Other ______

ug/L or mg/kg dry weight (Circle One)

1. Aluminum ____________
2. Antimony ____________
3. Arsenic ____________
4. Barium ____________
5. Beryllium ____________
6. Cadmium ____________
7. Calcium ____________
8. Chromium ____________
9. Cobalt ____________
10. Copper ____________
11. Iron ____________
12. Lead ____________
13. Magnesium ____________
14. Manganese ____________
15. Mercury ____________
16. Nickel ____________
17. Potassium ____________
18. Selenium ____________
19. Silver ____________
20. Sodium ____________
21. Thallium ____________
22. Vanadium ____________
23. Zinc ____________

Percent Solids (%) ____________

Footnotes: For reporting results, standard result qualifiers are used as defined on Cover Page. Additional flags or footnotes explaining results are encouraged. Definition of such flags must be explicit and contained on Cover Page, however.

Comments: ____
____
____
____

Lab Manager ______________

DOE - 5/87

Figure 2. Inorganic Analysis Data Sheet

Form II

Q.C. Report No. ________________

INITIAL AND CONTINUING CALIBRATION VERIFICATION[3]

Lab Name ________________________ Case No. ____________________

Date ____________________________ Units: ug/L

Compound	Initial Calibration			Continuing Calibration[2]					
Metals:	True Value	Found	%R	True Value	Found	%R	Found	%R	Method[4]
1. Aluminum									
2. Antimony									
3. Arsenic									
4. Barium									
5. Beryllium									
6. Cadmium									
7. Calcium									
8. Chromium									
9. Cobalt									
10. Copper									
11. Iron									
12. Lead									
[illegible]. Magnesium									
14. Manganese									
15. Mercury									
16. Nickel									
17. Potassium									
18. Selenium									
19. Silver									
20. Sodium									
21. Thallium									
22. Vanadium									
23 Zinc									
Other: ______									

[1] Initial Calibration Source ____________

[2] Continuing Calibration Source __________

[3] Control Limits: Mercury and Tin 80-120; Other Metals 90-110; Cyanide 85-115

[4] Indicate Analytical Method Used: P - ICP; A - Flame AA; F - Furnace AA;
CV - Cold Vapor AA

DOE - 5/87

Figure 3. Initial and Continuing Calibration Verification

Form III

Q.C. Report No. ____________________

BLANKS

Lab Name ______________________________ Case No. ___________________________

Date ________________________________ Units ______________________________

Compound	Initial Calibration Blank Value	Continuing Calibration Blank Value				Preparation Blank	
		1	2	3	4	Matrix: 1	Matrix: 2
Metals:							
1. Aluminum							
2. Antimony							
3. Arsenic							
4. Barium							
5. Beryllium							
6. Cadmium							
7. Calcium							
8. Chromium							
9. Cobalt							
10. Copper							
11. Iron							
12. Lead							
13. Magnesium							
14. Manganese							
15. Mercury							
16. Nickel							
17. Potassium							
18. Selenium							
19. Silver							
20. Sodium							
21. Thallium							
22. Vanadium							
23. Zinc							
Other: ________							

[1] Reporting Units: aqueous, ug/L; solid mg/kg

DOE - 5/87

Figure 4. Blanks

Form V

Q.C. Report No. ____________

SPIKE SAMPLE RECOVERY

Lab Name ______________________
Date ______________________

Case No. ______________________
DOE Sample No. ______________________
Lab Sample ID No. ______________________
Units ______________________

Matrix ______________

Compound	Control Limit %R	Spiked Sample Result (SSR)	Sample Result (SR)	Spiked Added (SA)	%R[1]
Metals:					
1. Aluminum	75-125				
2. Antimony	"				
3. Arsenic	"				
4. Barium	"				
5. Beryllium	"				
6. Cadmium	"				
7. Calcium	"				
8. Chromium	"				
9. Cobalt	"				
10. Copper	"				
11. Iron	"				
12. Lead	"				
13. Magnesium	"				
14. Manganese	"				
15. Mercury	"				
16. Nickel	"				
17. Potassium	"				
18. Selenium	"				
19. Silver	"				
20. Sodium	"				
21. Thallium	"				
22. Vanadium	"				
23. Zinc	"				
Other: ________					

[1] %R = [(SSR - SR)/SA] x 100
"N" - Out of control
"NR" - Not required
Comments: ____

DOE - 5/87

Figure 5. Spike Sample Recovery

92124571072

Form VI

Q.C. Report No. ____________

DUPLICATES

Lab Name ____________________________

Date ________________________________

Case No. ____________________________

DOE Sample No. ______________________

Lab Sample ID No. ___________________

Units _______________________________

Matrix ________________

Compound	Control Limit[1]	Sample (S)	Duplicate (D)	RPD[2]
Metals:				
1. Aluminum				
2. Antimony				
3. Arsenic				
4. Barium				
5. Beryllium				
6. Cadmium				
7. Calcium				
8. Chromium				
9. Cobalt				
10. Copper				
11. Iron				
12. Lead				
13. Magnesium				
14. Manganese				
15. Mercury				
16. Nickel				
17. Potassium				
18. Selenium				
19. Silver				
20. Sodium				
21. Thallium				
22. Vanadium				
23. Zinc				
Other: ________				

*Out of Control

[1] To be added at a later date.

[2] RPD - [|S - D|/((S + D)/2] x 100

NC - Non calculated RPD due to value(s) less than RDL.

DOE - 5/87

Figure 6. Duplicates

Form VII

Q.C. Report No. ________________

INSTRUMENT DETECTION LIMITS AND LABORATORY CONTROL SAMPLE

Lab Name ____________________ Case No. ____________________

Date ____________________ LCS No. ____________________

Compound	Required Detection Limits (CRDL)-ug/1		Instrument Detection Limits (IDL)-ug/1		Lab Control Sample ug/L mg/kg (circle one)		
	ICP/AA	Furnace/CV	ICP/AA ID#____	Furnace ID#____	True	Found	%R
Metals:							
1. Aluminum	200	--					
2. Antimony	150	60					
3. Arsenic	250	10					
4. Barium	200	--					
5. Beryllium	5	--					
6. Cadmium	20	5					
7. Calcium	5000	--					
8. Chromium	10	--					
Cobalt	50	--					
10. Copper	25	--					
11. Iron	100	--					
12. Lead	200	5					
13. Magnesium	5000	--					
14. Manganese	15	--					
15. Mercury	--	0.2					
16. Nickel	40	--					
17. Potassium	5000	--					
18. Selenium	400	5					
19. Silver	30	10					
20. Sodium	5000	--					
21. Thallium	200	10					
22. Vanadium	50	--					
23. Zinc	20	--					
Other: ________							

NR - Not required

DOE - 5/87

Figure 7. Instrument Detection Limits and Laboratory Control Sample

FORM X

Q.C. Report No. ____________________

HOLDING TIMES

Lab Name ______________________________ Case No. ___________________________

Date __________________________________

DOE Sample No.	Matrix	Date Received	Mercury Prep Date	Mercury Holding Time[1] (Days)	CN Prep Date	CN Holding Time[1] (Days)

[1] Holding time is defined as number of days between the date received and the sample preparation date.

DOE - 5/87

Figure 8. Holding Times

Form XIb (Quarterly)

INSTRUMENT DETECTION LIMITS - Furnace/Cold Vapor AA

Lab Name ______________________ Date ______________________

Furnace/Cold

Vapor AA Model Numbers ____________

Element	Wave-length (nm)	RDL (ug/L)	IDL (ug/L)	Element	Wave-length (nm)	RDL (ug/L)	IDL (ug/L)
1. Aluminum		NR		13. Magnesium		NR	
2. Antimony		60		14. Manganese		NR	
3. Arsenic		10		15. Mercury		0.2	
4. Barium		NR		16. Nickel		NR	
5. Beryllium		NR		17. Potassium		NR	
6. Cadmium		5		18. Selenium		5	
7. Calcium		NR		19. Silver		10	
8. Chromium		NR		20. Sodium		NR	
9. Cobalt		NR		21. Thallium		10	
10. Copper		NR		22. Vanadium		NR	
11. Iron		NR		23. Zinc		NR	
12. Lead		5					

Footnotes:

- Indicate the instrument for which the IDL applies with a "P" (for ICP), an "A" (for Flame AA), an "F" (for Furnace AA), or a "CV" (for Cold Vapor AA) behind the IDL value.
- Indicate elements commonly run with background correction (AA) with a "B" behind the analytical wavelength.
- If more than one ICP/Flame or Furnace AA is used, submit separate Forms XI-XIII for each instrument.

Comments: ____

____

____

Lab Manager ______________________

DOE 5/87

Figure 9. Instrument Detection Limits — Furnace/Cold Vapor AA

ANALYSIS OF HEXAVALENT CHROMIUM BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

(EPA Method 218.4)

1.0 SCOPE AND APPLICATION

1.1 This method covers the determination of dissolved hexavalent chromium (Cr^{+6}) in drinking, surface and saline waters. The method may also be applicable to certain domestic and industrial wastes after filtration provided that no interfering substances are present. (See Section 4.1.)

1.2 The method may be used to analyze samples containing from 1.0 to 25 ug Cr^{+6}/L.

2.0 SUMMARY OF METHOD

2.1 This method is based on the chelation of hexavalent chromium with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into the flame of the atomic absorption spectrophotometer.

2.2 Hexavalent chromium may also be chelated with pyrrolidine dithiocarbamic acid in chloroform. A pH of 2.3 must be maintained throughout the extraction.

2.3 The diphenylcarbazide colorimetric procedure as found on p. 201 of Standard Methods for the Examination of Water and Wastewater, 16th edition, 1985, may also be used.

3.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

3.1 Stability of hexavalent chromium is not completely understood at this time. Therefore, the chelation and extraction should be carried out as soon as possible.

INTERFERENCES

4.1 High concentrations of other reactive metals, as may be found in wastewaters, may interfere. The method is free from interferences from elements normally occurring in fresh water.

5.0 REAGENTS

5.1 Ammonium pyrrolidine dithiocarbamate (APDC) solution - Dissolve 1.0 g of APDC in demineralized water and dilute to 100 mL. Prepare fresh daily.

5.2 Bromphenol blue indicator solution - Dissolve 0.1 g of bromphenol blue in 100 mL of 50-percent ethanol.

5.3 Chromium standard solution I (1.0 mL = 100 ug Cr) - Dissolve 0.2829 g pure, dried $K_2Cr_2O_7$ in demineralized water and dilute to 1000 mL.

5.4 Chromium standard solution II (1.0 mL = 10.0 ug Cr) - Dilute 100 mL of chromium standard I to 1000 mL with demineralized water.

5.5 Chromium standard solution III (1.0 mL = 0.10 ug Cr) - Dilute 10.0 mL chromium standard solution II to 1000 mL with demineralized water.

5.6 Methyl isobutyl ketone (MIBK).

5.7 Sodium hydroxide solution (1 M) - Dissolve 40 g of NaOH in demineralized water and dilute to 1 L.

5.8 Sulfuric acid (0.12 M) - Slowly add 6.5 mL of concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 1 L.

6.0 PROCEDURE

6.1 The following instrumental parameters should be used for analysis:

Wavelength = 357.9 nm
Fuel = Acetylene
Oxidant = Air
Type of Flame = Fuel rich (adjust for organic solvent).

6.2 Pipet a volume of sample containing less than 2.5 ug chromium (100 mL maximum) into a 200-mL volumetric flask, and adjust the volume to approximately 100 mL.

6.3 Prepare a blank and sufficient standards, and adjust the volume of each to approximately 100 mL.

6.4 Add 2 drops of bromphenol blue indicator solution. (The pH adjustment to 2.4 may also be made with a pH meter instead of using an indicator.)

6.5 Adjust the pH by addition of 1 M NaOH solution dropwise until a blue color persists. Add 0.12 M H_2SO_4 dropwise until the blue color just disappears in both the standards and sample. Then add 2.0 mL of 0.12 M H_2SO_4 in excess. The pH at this point should be 2.4.

6.6 Add 5.0 mL of APDC solution and mix. The pH should then be approximately 2.8.

6.7 Add 10.0 mL of MIBK and shake vigorously for 3 min.

6.8 Allow the layers to separate and add demineralized water until the ketone layer is completely in the neck of the flask.

6.9 Aspirate the ketone layer and record the scale reading for each sample and standard against the blank. Repeat, and average the duplicate results.

7.0 CALCULATIONS

7.1 Determine the ug Cr^{+6}/L in each sample from a plot of scale readings of standards. A working curve must be prepared with each set of samples. Report Cr^{+6} concentrations as follows: Less than 10 ug/L, nearest ug/L; 10 ug/L and above, two significant figures.

8.0 PRECISION AND ACCURACY

8.1 In a single laboratory (EPA's Environmental Monitoring and Support Laboratory), using the APDC extraction procedure to analyze tap water spiked at a concentration of 50 ug Cr^{+6}/L, the standard deviation was ±2.6 with a mean recovery of 96 percent.

NON-TARGET
LIST
PARAMETERS

OTHER ORGANICS

OIL AND GREASE
(EPA Method 413.1)

1.0 SCOPE AND APPLICATION

1.1 This method includes the measurement of fluorocarbon-113 extractable matter from surface and saline waters and industrial and domestic waste. It is applicable to the determination of relatively non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases, and related matter.

1.2 The method is not applicable to the measurement of light hydrocarbons that volatilize at temperatures below 70°C. Petroleum fuels from gasoline through fuel oils are completely or partially lost in the solvent removal operation.

1.3 Some crude oils and heavy fuel oils contain a significant percentage of residue-type materials that are not soluble in fluorocarbon-113. Accordingly, recoveries of these materials will be low.

1.4 The method covers the range from 5 to 1000 mg/L of extractable material.

2.0 SUMMARY OF METHOD

The sample is acidified to a low pH (<2) and serially extracted with fluorocarbon-113 in a separatory funnel. The solvent is evaporated from the extract and the residue weighed.

3.0 DEFINITIONS

3.1 The definition of oil and grease is based on the procedure used. The nature of the oil or grease and the presence of extractable non-oily matter will influence the material measured and interpretation of results.

4.0 SAMPLING COLLECTION, PRESERVATION, AND HANDLING

4.1 A representative 1-L sample should be collected in a glass bottle. If analysis is to be delayed for more than a few hours, the sample is preserved by adding 5 mL of hydrochloric acid (1 + 1) (Section 6.1) at the time of collection and refrigerated at 4°C.

4.2 Because loss of grease will occur on sampling equipment, the collection of a composite sample is impractical. Individual portions collected at prescribed time intervals must be analyzed separately to obtain the average concentration over an extended period.

5.0 APPARATUS AND EQUIPMENT

5.1 Separatory funnel - 2000 mL, with Teflon stopcock.
5.2 Vacuum pump, or other source of vacuum.
5.3 Boiling flask - 125 mL (Corning No. 4100 or equivalent).
5.4 Distilling head - Claisen or equivalent.
5.5 Filter paper - Whatman No. 40, 11 cm.

6.0 REAGENTS

6.1 Hydrochloric acid (1 + 1) - Mix equal volumes of concentrated HCl and distilled water.

6.2 Fluorocarbon-113 - (1,1,2-trichloro-1,2,2-trifluoroethane), b.p. 48°C.

6.3 Sodium sulfate - Anhydrous crystal.

7.0 PROCEDURE

7.1 Mark the sample bottle at the water meniscus for later determination of sample volume. If the sample was not acidified at the time of collection, add 5 mL of hydrochloric acid (1+1) to the sample bottle. After mixing the sample, check the pH by touching pH-sensitive paper to the cap to insure that the pH is 2 or lower. Add more acid if necessary.

7.2 Pour the sample into a separatory funnel.

7.3 Tare a boiling flask (pre-dried in an oven at 130°C and stored in a desiccator).

7.4 Add 30 mL of fluorocarbon-113 to the sample bottle, and rotate the bottle to rinse the sides. Transfer the solvent into the separatory funnel. Extract by shaking vigorously for 2 min. Allow the layers to separate, and filter the solvent layer into the flask through a funnel containing solvent-moistened filter paper.

Note: An emulsion that fails to dissipate can be broken by pouring about 1 g of sodium sulfate into the filter paper cone and slowly draining the emulsion through the salt. Additional 1-g portions can be added to the cone as required.

7.5 Repeat Section 7.4 twice more with additional portions of fresh solvent, combining all solvent in the boiling flask.

7.6 Rinse the tip of the separatory funnel, the filter paper, and then the funnel with a total of 10 to 20 mL of solvent, and collect the rinsings in the flask.

7.7 Connect the boiling flask to the distilling head, and evaporate the solvent by immersing the lower half of the flask in water at 70°C. Collect the solvent for re-use. A solvent blank should accompany each set of samples.

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7.8 When the temperature in the distilling head reaches 50°C, or the flask appears dry, remove the distilling head. Sweep out the flask for 15 s with air to remove solvent vapor by inserting a glass tube connected to a vacuum source. Immediately remove the flask from the heat source and wipe the outside to remove excess moisture and fingerprints.

7.9 Cool the boiling flask in a desiccator for 30 min and weigh.

8.0 CALCULATION

$$\text{Total oil and grease (mg/L)} = \frac{R - B}{V}$$

where:

R = Residue, gross weight of extraction flask minus the tare weight (mg)

B = Blank determination, residue of equivalent volume of extraction solvent (mg)

V = Volume of sample, determined by refilling sample bottle to calibration line and correcting for acid addition if necessary (L).

9.0 PRECISION AND ACCURACY

The oil and grease method was tested on sewage by the EPA's Environmental Monitoring Systems Laboratory in Las Vegas (EMSL-LV). This method determined the oil and grease level in the sewage to be 12.6 mg/L. When 1-L portions of the sewage were dosed with 14.0 mg of a mixture of No. 2 fuel oil and Wesson oil, the recovery was 93 percent with a standard deviation of 0.9 mg/L.

10.0 REFERENCES

1. _Standard Methods for the Examination of Water and Wastewater_, 16th Edition, Method 503A, 1985, p. 497.

2. Blum, K. A., and M. J. Taras. "Determination of Emulsifying Oil in Industrial Wastewater," _JWPCF Research Suppl._ _40_, R404, 1968.

TOTAL ORGANIC CARBON
(EPA Method 415.1)

1.0 SCOPE AND APPLICATION

1.1 This method includes the measurement of organic carbon in drinking, surface, and saline waters and domestic and industrial waste. Exclusions are noted in Sections 3.0 and 4.0.

1.2 The method is most applicable to measurements of organic carbon above 1 mg/L.

2.0 SUMMARY OF METHOD

2.1 Organic carbon in a sample is converted to carbon dioxide (CO_2) by catalytic combustion or wet chemical oxidation. The CO_2 formed can be measured directly by an infrared detector or converted to methane (CH_4) and measured by a flame ionization detector. The amount of CO_2 or CH_4 is directly proportional to the concentration of carbonaceous material in the sample.

3.0 INTERFERENCES

3.1 Carbonate and bicarbonate carbon represent an interference under the terms of this test and must be removed or accounted for in the final calculation.

3.2 This procedure is applicable only to homogeneous samples that can be injected into the apparatus reproducibly by means of a syringe or pipet. The openings of the syringe or pipet limit the maximum size of particles that may be included in the sample.

4.0 DEFINITIONS

4.1 The carbonaceous analyzer measures all of the carbon in a sample. Because of various properties of carbon-containing compounds in liquid samples, preliminary treatment of the sample prior to analysis dictates the definition of the carbon as it is measured. Forms of carbon that are measured by the method are:

1. Soluble, nonvolatile organic carbon (e.g., natural sugars).

2. Soluble, volatile organic carbon (e.g., mercaptans).

3. Insoluble, partially volatile carbon (e.g., oils).

4. Insoluble, particulate carbonaceous materials (e.g., cellulose fibers).

5. Soluble or insoluble carbonaceous materials adsorbed or entrapped on insoluble organic suspended matter (e.g., oily matter adsorbed on silt particles).

4.2 The final usefulness of the carbon measurement is in assessing the potential oxygen-demanding load of organic material on a receiving stream. This statement applies whether the carbon measurement is made on sewage plant effluent industrial waste or on water taken directly from the stream. In this light, carbonate and bicarbonate carbon are not a part of the oxygen demand in the stream and therefore should be discounted in the final calculation or removed prior to analysis. The manner or preliminary treatment of the sample and instrument settings defines the type of carbon measured. Instrument manufacturer's instructions should be followed.

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

5.1 Sampling and storing samples in glass bottles is preferable. Sampling and storing in plastic bottles (such as conventional polyethylene and cubitainers) is permissible if it is established that the containers do not contribute contaminating organics to the samples.

Note: A brief study performed in an EPA laboratory indicated that distilled water stored in new, 1-qt cubitainers did not show any increase in organic carbon after two weeks' exposure.

5.2 Because of the possibility of oxidation or bacterial decomposition of some components of aqueous samples, the lapse of time between the collection of samples and the start of analysis should be kept to a minimum. Also, samples should be kept cool (4°C) and protected from sunlight and atmospheric oxygen.

5.3 In instances where analysis cannot be performed within 2 h from the time of sampling, the sample is acidified (pH <2) with hydrochloric or sulfuric acid.

6.0 APPARATUS AND EQUIPMENT

6.1 For blending or homogenizing samples, a Waring-type blender is generally satisfactory.

6.2 For total and dissolved organic carbon:

1. A number of companies manufacture systems for measuring carbonaceous material in liquid samples. The type of samples to be analyzed, the expected concentration range, and the form of carbon to be measured should be considered.
2. No specific analyzer is recommended as superior.

7.0 REAGENTS

7.1 Distilled water used in preparing of standards and diluting samples should be ultrapure to reduce the carbon concentration of the blank. Carbon dioxide-free, double-distilled water is recommended. Ion-exchanged water is not recommended because of the possibility of contamination with organic material from the resins.

7.2 Potassium hydrogen phthalate stock solution (1000 mg carbon/L) - Dissolve 0.2128 g of potassium hydrogen phthalate (primary standard grade) in distilled water and dilute to 100.0 mL.

Note: Sodium oxalate and acetic acid are not recommended as stock solutions.

7.3 Potassium hydrogen phthalate standard solution - Prepare the standard solution from the stock solution by dilution with distilled water.

7.4 Carbonate-bicarbonate stock solution (1000 mg carbon/L) - Weigh 0.3500 g of sodium bicarbonate and 0.4418 g of sodium carbonate and transfer both to the same 100-mL volumetric flask. Dissolve with distilled water.

7.5 Carbonate-bicarbonate standard solution - Prepare a series of standards similar to Section 7.3.

Note: This standard is not required by some instruments.

7.6 Blank solution - Use the same distilled water (or a similar quality of water) used for preparing the standard solution.

8.0 PROCEDURE

8.1 Follow instrument manufacturer's instructions for calibration, procedure, and calculations.

8.2 For calibration of the instrument, a series of standards encompassing the expected concentration range of the samples is recommended.

.0 PRECISION AND ACCURACY

Twenty-eight analysts in 21 laboratories analyzed distilled water solutions containing exact increments of oxidizable organic compounds, with the following results.

Increment as TOC (mg/L)	Precision as Standard Deviation (mg/L)	Accuracy as Bias (%)	Accuracy as Bias (mg/L)
4.9	3.93	+15.27	+0.75
107	8.32	+ 1.01	+1.08

(FWPCA Method Study 3, Demand Analyses)

10.0 REFERENCES

1. Annual Book of ASTM Standards, Part 34. "Water" (Standard 1) 2574-79, 1976, p. 469.

2. Standard Methods for the Examination of Water and Wastewater, 16th Edition, Method 505, 1985, p. 508.

OTHER INORGANICS

TOTAL CYANIDE
(EPA Method 335.2)

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the determination of cyanide in drinking, surface, and saline waters and domestic and industrial waste.

1.2 The titration procedure using silver nitrate with p-dimethylamino-benzal-rhodanine indicator is used for measuring concentrations of cyanide exceeding 1 mg/L (0.25 mg/250 mL of absorbing liquid).

1.3 The colorimetric procedure used for concentrations below 1 mg/L of cyanide is sensitive to about 0.02 mg/L.

2.0 SUMMARY OF METHOD

2.1 Cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by volumetric titration or colorimetrically.

2.2 In the colorimetric measurement, cyanide is converted to cyanogen chloride, CNCl, by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-pyrazolone or pyridine barbituric acid reagent. The absorbance is read at 620 nm when using pyridine-pyrazolone or 578 nm for pyridine-barbituric acid. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.

2.3 The titrimetric measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver-sensitive indicator.

3.0 INTERFERENCES

3.1 Interferences are eliminated or reduced by using the distillation procedure described in Sections 8.1 through 8.5.

3.2 Sulfides adversely affect the colorimetric and titration procedures. If a drop of the distillate on lead acetate test paper indicates the presence of sulfides, treat 25 mL more of the sample than that required for the cyanide determination with powdered cadmium carbonate. Yellow cadmium sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution through a dry filter paper into a dry beaker, and from the filtrate, measure the sample to be used for analysis. Avoid a large excess of cadmium and a long contact time in order to minimize a loss by complexation or occlusion of cyanide on the precipitated material. Sulfides should be removed prior to preservation with sodium hydroxide as described in Section 5.3.

3.3 Fatty acids will distill and form soaps under alkaline titration conditions, making the end point almost impossible to detect.

3.3.1 Acidify the sample with acetic acid (1+9) to pH 6.0 to 7.0. Caution: This operation must be performed in the hood and the sample left there until it can be made alkaline again after the extraction has been performed.

3.3.2 Extract with iso-octane, hexane, or chloroform (in the order named) with a solvent volume equal to 20 percent of the sample volume. One extraction is usually adequate to reduce the fatty acids below the interference level. Avoid multiple extractions or a long contact time at low pH in order to keep the loss of HCN at a minimum. When the extraction is complete, immediately raise the pH of the sample to above 12 with NaOH solution.

.0 DEFINITIONS

4.1 Cyanide is defined as cyanide ion and complex cyanides converted to hydrocyanic acid (HCN) by reaction in a reflux system of a mineral acid in the presence of magnesium ion.

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

5.1 The sample should be collected in plastic or glass bottles of 1-L volume or larger. All bottles must be thoroughly cleansed and thoroughly rinsed to remove soluble material.

5.2 Oxidizing agents such as chlorine decompose most of the cyanides. Test a drop of the sample with potassium iodide-starch test paper (KI-starch paper); a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper. Then add an additional 0.6 g of ascorbic acid for each liter of sample volume.

5.3 Samples must be preserved with 2 mL of 10 N sodium hydroxide per liter of sample (pH $\geq$ 12) at the time of collection.

5.4 Samples should be analyzed as rapidly as possible after collection. If storage is required, the samples should be stored in a refrigerator or in an ice chest filled with water and ice to maintain a temperature of 4°C.

6.0 APPARATUS AND EQUIPMENT

6.1 Reflux distillation apparatus such as shown in Figure 1 or Figure 2 - The boiling flask should be 1-L volume with an inlet tube and provision for a condenser. The gas absorber may be a Fisher-Milligan scrubber.

6.2 Microburet - 5.0 mL (for titration).

6.3 Spectrophotometer - Suitable for measurements at 578 nm or 620 nm with a 1.0-cm cell or larger.

7.0 REAGENTS

7.1 Sodium hydroxide solution (1.25N) - Dissolve 50 g of NaOH in distilled water, and dilute to 1 L with distilled water.

7.2 Cadmium carbonate - Powdered.

7.3 Ascorbic acid - Crystals.

7.4 Dilute sodium hydroxide solution (0.25N) - Dilute 200 mL of 1.25 N sodium hydroxide solution to 1000 mL with distilled water.

7.5 Sulfuric acid - Concentrated.

7.6 Sodium dihydrogenphosphate (1 M) - Dissolve 138 g of NaH_2PO_4 H_2 in 1 L of distilled water. Refrigerate.

7.7 Stock cyanide solution (1 mg CN/mL) - Dissolve 2.51 g of KCN and 2 g KOH in 1 L of distilled water. Standardize with 0.0192 N $AgNO_3$. Dilute to appropriate concentration.

7.8 Intermediate standard cyanide solution (50 ug CN/mL) - Dilute 50.0 mL of stock cyanide solution to 1000 mL with distilled water.

7.9 Working standard cyanide solution (5.0 mg/L) - Prepare fresh daily by diluting 100.0 mL of intermediate cyanide solution to 1000 mL with distilled water and store in a glass-stoppered bottle.

7.10 Standard silver nitrate solution (0.0192 N) - Prepare by crushing approximately 5 g of $AgNO_3$ crystals and drying to constant weight at 40°C. Weigh out 3.2647 g of dried $AgNO_3$, dissolve in distilled water, and dilute to 1000 mL (1 mL = 1 mg CN).

7.11 Rhodanine indicator - Dissolve 20 mg of p-dimethyl-aminobenzalrhodanine in 100 mL of acetone.

7.12 Chloramine T solution - Dissolve 1.0 g of white, water-soluble Chloramine T in 100 mL of distilled water, and refrigerate until ready to use. Prepare fresh weekly.

7.13 Color reagent - One of the following may be used:

7.13.1 Pyridine-barbituric acid reagent - Place 15 g of barbituric acid in a 250-mL volumetric flask and add just enough distilled water to wash the sides of the flask and wet the barbituric acid. Add 75 mL of pyridine and mix. Add 15 mL of hydrochloric acid (sp gr 1.19), mix, and cool to room temperature. Dilute to 250 mL with distilled water and mix. This reagent is stable for approximately six months if stored in a cool dark place.

7.13.2 Pyridine-pyrazolone solution

7.13.2.1 3-Methyl-1-phenyl-2-pyrazoline-5-one reagent, saturated solution - Add 0.25 g of 3-methyl-1-phenyl-2-pyrazoline-5-one to 50 mL of distilled water, heat to 60°C while stirring. Cool to room temperature.

7.13.2.2 3,3-Dimethyl-1, 1'-diphenyl-[4,4'-bi-2 pyrazoline]-5,5'dione (bispyrazolone) - Dissolve 0.01 g of bispyrazolone in 10 mL of pyridine.

7.13.2.3 Pour the solution in Section 7.13.2.1 through non-acid-washed filter paper. Collect the filtrate. Through the same filter paper, pour the solution in Section 7.13.2.2, collecting the filtrate in the same container as filtrate from Section 7.13.2.1. Mix until the filtrates are homogeneous. The mixed reagent develops a pink color, but this does not affect the color production with cyanide if used within 24 h of preparation.

7.14 Magnesium chloride solution - Weigh 510 g of $MgCl_2 \cdot 6H_2O$ into a 1000-mL flask, dissolve, and dilute to 1 L with distilled water.

8.0 PROCEDURE

8.1 Place 500 mL of sample, or an aliquot diluted to 500 mL in the 1-L boiling flask. Add 50 mL of 1.25 N sodium hydroxide solution to the absorbing tube, and dilute if necessary with distilled water to obtain an adequate depth of liquid in the absorber. Connect the boiling flask, condenser, absorber, and trap in the train.

8.2 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately one bubble of air per second enters the boiling flask through the air inlet tube.

Caution: The bubble rate will not remain constant after the reagents have been added and while heat is being applied to the flask. It will be necessary to readjust the air rate occasionally to prevent the solution in the boiling flask from backing up into the air inlet tube.

8.3 Slowly add 24 mL of concentrated sulfuric acid through the air inlet tube. Rinse the tube with distilled water, and allow the airflow to mix the flask contents for 3 min. Pour 20 mL of magnesium chloride solution into the air inlet and wash down with a stream of water.

8.4 Heat the solution to boiling, taking care to prevent the solution from backing up into and overflowing from the air inlet tube. Reflux for one hour. Turn off heat and continue the airflow for at least 15 min. After cooling the boiling flask, disconnect absorber and close off the vacuum source.

8.5 Drain the solution from the absorber into a 250-mL volumetric flask and bring up to volume with distilled water washings from the absorber tube.

8.6 Withdraw 50 mL or less of the solution from the flask and transfer to a 100-mL volumetric flask. If less than 50 mL is taken, dilute to 50 mL with 0.25 N sodium hydroxide solution. Add 15.0 mL of sodium dihydrogenphosphate and mix.

8.6.1 Pyridine-barbituric acid method - Add 2 mL of Chloramine T solution and mix. After 1 to 2 min, add 5 mL of pyridine-barbituric acid solution and mix. Dilute to mark with distilled water and mix again. Allow 8 min for color development, then read absorbance at 578 mm in a 1-cm cell within 15 min.

8.6.2 Pyridine-pyrazolone method - Add 0.5 mL of Chloramine T solution and mix. After 1 to 2 min, add 5 mL of pyridine-pyrazolone solution and mix. Dilute to mark with distilled water and mix again. After 40 min, read absorbance at 620 nm in a cell.

Note: More than 0.5 mL of Chloramine T solution will prevent the color from developing with pyridine-pyrazolone.

8.7 Prepare a series of standards by pipeting suitable volumes of standard solution into 250-mL volumetric flasks. To each standard, add 50 mL of 1.25 N sodium hydroxide solution and dilute to 250 mL with distilled water. Prepare as follows:

Volume of Standard Solution Used (mL)	Concentration of Standard (ug CN/mL)
0	Blank
1.0	5
2.0	10
5.0	25
10.0	50
15.0	60
20.0	100

8.7.1 It is not imperative that all standards be distilled in the same manner as the samples. It is recommended that at least two standards (a high and low) be distilled and compared to similar values on the curve to ensure that the distillation technique is reliable. If distilled standards do not agree within ±10 percent of the undistilled standards, the operator should find the cause of the apparent error before proceeding.

8.7.2 Prepare a standard curve by plotting absorbance of standard vs. cyanide concentrations.

8.7.3 To check the efficiency of the sample distillation, add an increment of cyanide from either the intermediate standard cyanide solution or the working standard cyanide solution to ensure a level of 20 g/L or a significant increase in absorbance value. Proceed with the analysis as in Section 8.1 using the same flask and system from which the previous sample was just distilled.

8.8 Alternatively, if the sample contains more than 1 mg of CN, transfer the distillate or a suitable aliquot diluted to 250 mL, to a 500-mL Erlenmeyer flask. Add 10 to 12 drops of the rhodanine indicator.

8.9 Titrate with standard silver nitrate solution to the first change in color from yellow to brownish-pink. Titrate a distilled water blank using the same amount of sodium hydroxide and indicator as in the sample.

8.10 The analyst should familiarize himself with the end point of the titration and the amount of indicator to be used before actually titrating the samples. A 5- or 10-mL microburet may be conveniently used to obtain a more precise titration.

9.0 CALCULATIONS

9.1 If the colorimetric procedure is used, calculate the cyanide in the original sample using the following equation.

$$\text{CN (ug/L)} = \frac{A \times 1000 \times 50}{B \times C}$$

where:

A = CN read from standard curve (ug)
B = Volume of original sample for distillation (mL)
C = Volume taken for colorimetric analysis (mL).

9.2 Using the titrimetric procedure, calculate concentration of CN using the following equation:

$$\text{CN (mg/L)} = \frac{(A - B)1000}{C} \times \frac{250}{D}$$

where:

A = Volume of $AgNO_3$ for titration of sample (mL)
B = Volume of $AgNO_3$ for titration of blank (mL)
C = Volume of original sample (mL)
D = Volume of aliquot titrated (mL).

10.0 PRECISION AND ACCURACY

10.1 In a single laboratory (EMSL), using mixed industrial and domestic waste samples at concentrations of 0.06, 0.13, 0.28 and 0.62 mg/L CN, the standard deviations were ±0.005, ±0.0007, ±0.031 and ±0.094, respectively.

10.2 In a single laboratory (EMSL), using mixed industrial and domestic waste samples at concentrations of 0.28 and 0.62 mg/L CN, recoveries were 85 percent and 102 percent, respectively.

11.0 REFERENCES

1. Bark, L. S., and H. G. Higson. "Investigation of Reagents for the Colorimetric Determination of Small Amounts of Cyanide," *Talanta*, 2:471-479, 1964.

2. Elly, C. T. "Recovery of Cyanides by Modified Serfass Distillation" *Journal Water Pollution Control Federation*, 40:848-856, 1968.

3. *Annual Book of ASTM Standards*, Part 31. "Water," Standard D2036-75. Method A, 1976, p. 503.

4. *Standard Methods for the Examination of Water and Wastewater*, 16th Edition, Method 412B,C, and D, 1985, pp. 334-338.

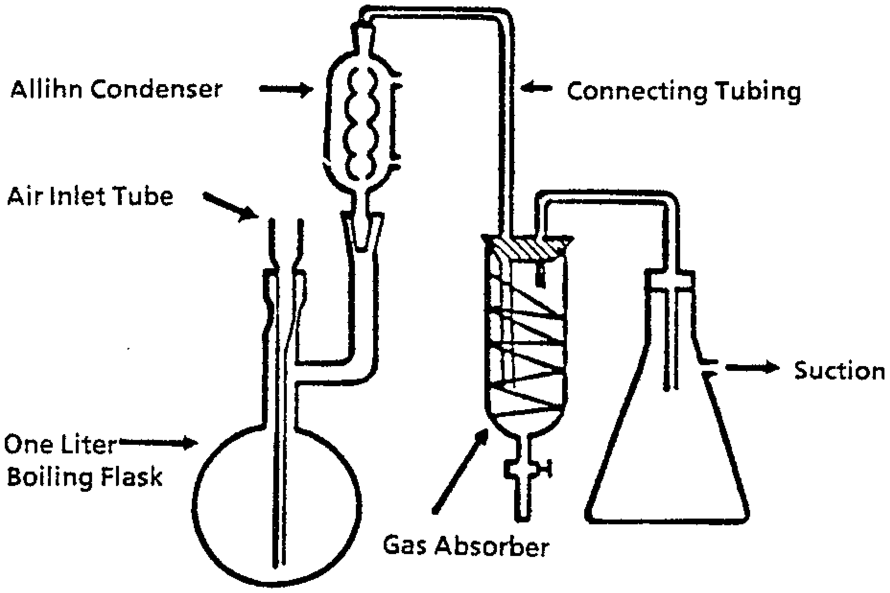
Allihn Condenser
Connecting Tubing
Air Inlet Tube
Suction
One Liter Boiling Flask
Gas Absorber

Figure 1. Cyanide Distillation Apparatus

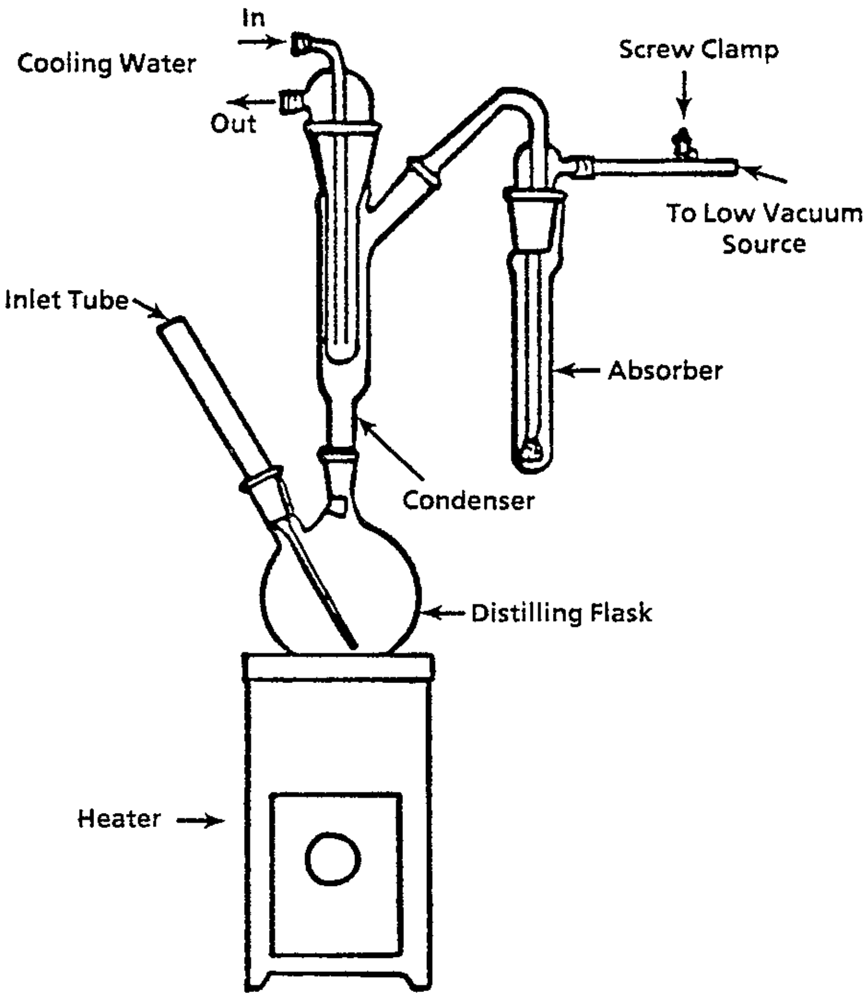
In
Cooling Water
Out
Screw Clamp
To Low Vacuum Source
Inlet Tube
Absorber
Condenser
Distilling Flask
Heater

Figure 2. Cyanide Distillation Apparatus

HYDROGEN CYANIDE AND HYDROGEN SULFIDE

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to water, wastewater, and industrial waste.

1.2 The method provides a fast and simple method to determine if a waste is reactive as a result of its tendency to release toxic levels of hydrogen cyanide or hydrogen sulfide upon contact with acidic medium. The approach is based on a reasonable worst case disposal scenario.

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1.3 This method is designed to measure only the hydrogen cyanide or hydrogen sulfide gas evolved at the test conditions and not to reflect the total concentration of these gases, or their precursors, in the sample. Variations in temperature, ionic strength, and total volume of the test solution will affect the amount of gas evolved. The total volume of the test solution will affect the amount of gas evolved. The total volume of solution is kept constant from test to test. Ionic strength is not controlled as it is an inherent property of each waste. In this method, test solutions are not purged with a gas because this would not reflect disposal conditions.

2.0 SUMMARY OF METHOD

2.1 An aliquot of the waste is acidified to pH 2 in a closed system. The gas generated is swept from the reaction chamber using a pump and passed through a calibrated gas detector tube. The detector tube reading is used to calculate the amount of toxic gas evolved per gram (or mL) of waste.

3.0 INTERFERENCES

3.1 The analyst should consult manufacturers' literature on the type and nature of potential interferences when using specific detector tubes.

4.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

4.1 Samples containing, or suspected of containing sulfide or a combination of sulfide and cyanide waste, should be collected with a minimum of aeration. The sample bottle should be filled completely, excluding all head space, and stoppered. Analysis should commence as soon as possible; and samples should be kept in a cool, dark place until analysis begins.

4.2 Samples containing, or suspected of containing cyanide waste without the presence of sulfide compounds, can be preserved if analysis cannot begin immediately. Samples are preserved by adjusting them to pH 12 with strong sodium hydroxide solution and storing them in a cool, dark place.

4.3 Determinations should be performed in a well-ventilated hood.

5.0 APPARATUS AND EQUIPMENT

5.1 Flask - 250 mL, three-neck, round-bottom, with 24/40 ground-glass joints.

5.2 Magnetic stirring bar - With magnetic stirring apparatus.

5.3 Separatory funnel - 125 mL, with pressure-equalizing tube and 24/40 ground-glass joint.

5.4 Adapter tubes - Straight, glass with 24/40 ground-glass joint and rubber adapter sleeve.

5.5 Flexible tubing - To make connection from detector tube to pump.

5.6 Detector tubes - HCN detector tube with a range of 10 to 12 uL (Draeger 67-28441 or equivalent). H_2S detector tube with a range of 5 to 60 uL (Draeger 67-28141 or equivalent).

5.7 pH meter and pH electrode - Of sufficient length to reach liquid level (approximately 18 cm).

5.8 Pump - Capable of pulling 60 mL/min (MSA Corporation Model C-210 or equivalent).

5.9 Bubble meter - For calibrating pump.

5.10 Stopwatch.

6.0 REAGENTS

6.1 Sulfuric acid - (1 N).

6.2 Cyanide reference solution (1 mg/mL) - Dissolve approximately 2.5 g of KOH and 2.51 g of KCN in 1 L of distilled water.

6.3 Sulfide reference solutions - Prepare from crystals of sodium sulfide as described in Method 376.2 (sulfide, colorimetric, methylene blue) Section 5.8 of "Methods for Chemical Analysis of Water and Wastes," EPA 600/4-79-020, March 1979. The solution may be standardized by the titrimetric iodine method (376.1) of the same publication, although this is not required.

7.0 PROCEDURE

7.1 The operation of the system can be checked using the cyanide or sulfide reference solutions. It is difficult to predict a detector tube reading from a known amount of reference solution due to variations in the response of detector tubes of total volumes also influence the amount of gases evolved. However, the reference solutions can be used to verify system operation, and replicates can be expected to agree to within approximately ±20 percent.

7.2 Place 10 g (or mL) of the material to be analyzed into a beaker. In a well-ventilated hood, add approximately 80 mL of deionized water and determine the amount of sulfuric acid required to adjust the solution pH to 2.0.

7.3 Place a second 10 g (or mL) aliquot of the waste into the 250-mL, round-bottom flask. Add deionized water in an amount so that the sum of the volume of water and the volume of sulfuric acid, required for pH adjustment, will equal 100 mL.

7.4 Assemble the apparatus as shown in Figure 1 using the proper detection tube and tubes.

7.5 Calibrate the pump in line to a flow of 60 ± 3 mL/min using the bubble meter attached to the pump outlet. Measure the flow before and after the test period.

7.5.1 Begin stirring the sample, and make sure all connections are tight.

7.5.2 Carefully adjust the test solution to pH 2.0 using the 1 N H_2SO_4.

Note: Take readings of stain length at 5-min intervals. If the length of the stain exceeds the capacity of the detector tube, re-analyze the sample using a smaller aliquot. If very little or no stain develops, the aliquot size may be increased, depending on the nature of the sample. Solid samples require a certain amount of dilution to reach a slurry state so that the acid may contact all portions of the sample and so that stirring may take place.

7.6 After 30 min, stop the pump and record the final detector tube reading.

Note: The chemistry of some detector tubes may permit their use in a series to determine both H_2S and HCN concurrently. When tests were conducted (by the EAL Corporation) with Draeger detector tubes, the H_2S tube had to be placed in front of the HCN tube for satisfactory results. Detector tubes from other manufacturers may perform differently.

Note: As an operational step (to determine a total evoluable gas value) at the end of the 30-min test, the pH can be lowered to less than pH 1 and a sand bath used to elevate the temperature. Increased evolution rates may be observed from some samples.

8.0 CALCULATIONS

8.1 HCN evolved (ug) = Stain tube reading (uL) x 1.1 ug/uL

8.2 H_2S evolved (ug) = Stain tube reading (uL) x 1.4 ug/uL

8.3 HCN or H S evolved (ug/mL or ug/g) = HCN or H_2S evolved (ug)/Volume of sample aliquot (g or mL)

8.4 Total gas volume pumped through stain tube can be calculated using the following equation.

$$\text{Total gas volume (L)} = \frac{F_1 + F_2}{2} \times \frac{T}{1000}$$

where:

F_1 = Pump flow rate before the analysis (mL/min)
F_2 = Pump flow rate after the analysis (mL/min)
T = Time duration of pumping (min).

8.5 The time of maximum gas evolution rate for a sample can be determined by relating the largest measurement change between 5-min periods to the elapsed time.

9.0 PRECISION AND ACCURACY

9.1 Relative standard deviations for the method were found by an interlaboratory study to be 17 percent for HCN (at the 27-uL level) and 24 percent for H_2S (at the 24-uL level).

9.2 The accuracy of the method cannot be determined directly due to the difficulty of providing a sample of known gas evolution qualities. Calibration of the detector tubes used in this method with standard gas mixtures indicates the bias of the H_2S tubes to be approximately 16 percent positive at 20°C and the bias of the HCN tubes to be approximately 35 percent at 20°C.

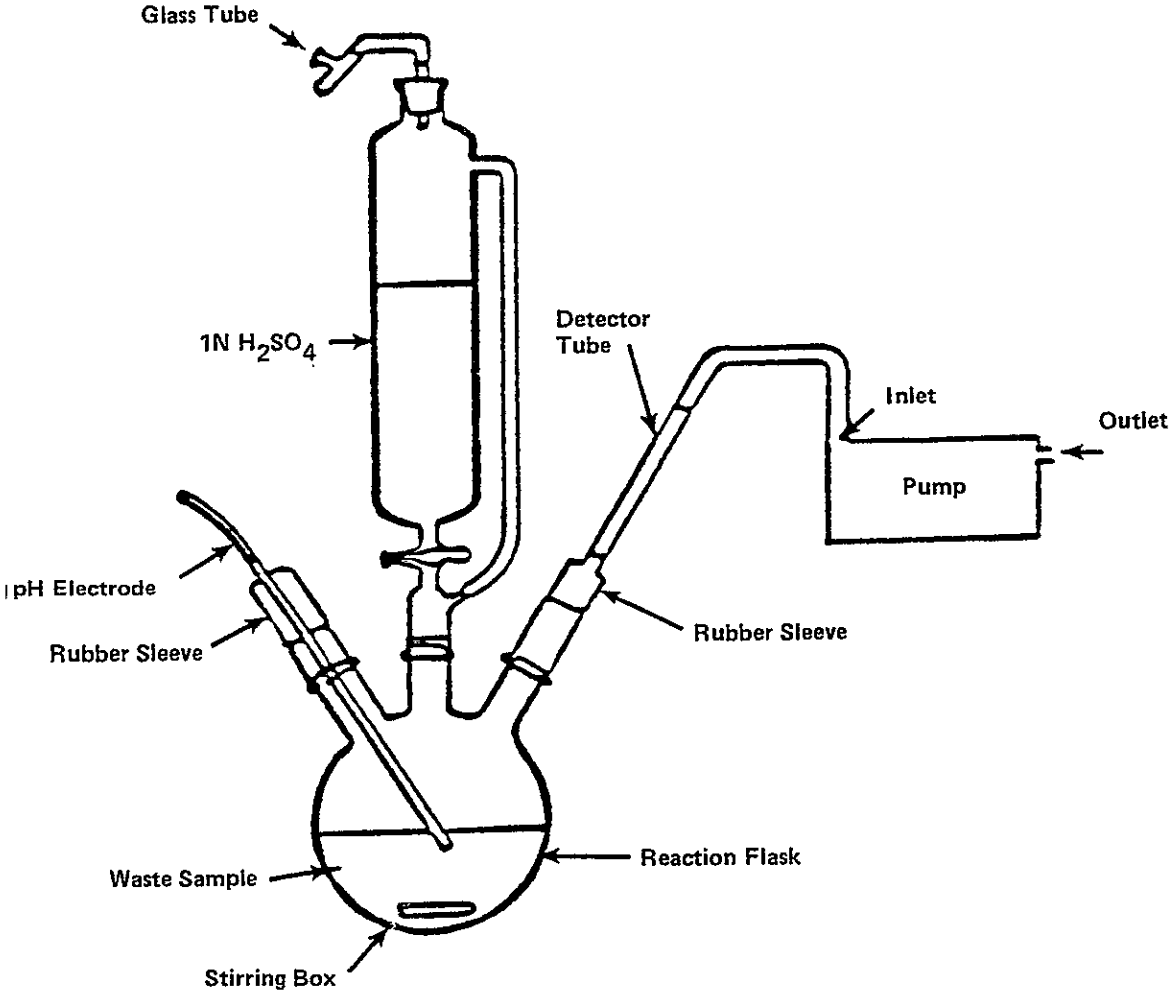
Glass Tube
1N H_2SO_4
Detector Tube
Inlet
Outlet
Pump
pH Electrode
Rubber Sleeve
Rubber Sleeve
Reaction Flask
Waste Sample
Stirring Box

Figure 1. Test Apparatus

CHLORINE, TOTAL RESIDUAL
(EPA Method 330.5)

1.0 SCOPE AND APPLICATION

1.1 The DPD-colorimetric method is applicable to natural and treated waters at concentrations from 0.2 to 4 mg/L.

2.0 SUMMARY OF METHOD

2.1 Chlorine (hypochlorite ion, hypochlorous acid) and chloramines stoichiometrically liberate iodine from potassium iodine at pH 4 or less. The liberated iodine reacts with N,N-diethyl-p-phenylene diamine (DPD) to produce a red-colored solution. The solution is spectrophotometrically compared to a series of standards, using a graph or a regression analysis calculation. The results are read or calculated into mg/L Cl.

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3.0 INTERFERENCES

3.1 Any oxidizing agents; these are usually present at insignificant concentrations compared to the residual chlorine concentrations.

3.2 Turbidity and color will essentially prevent the colorimetric analysis.

4.0 APPARATUS AND EQUIPMENT

4.1 Spectrophotometer for use at 515 nm and cells of light path 1 cm or longer.

5.0 REAGENTS

5.1 Phosphate buffer solution - Dissolve 24 g of anhydrous disodium hydrogen phosphate, Na_2HPO_4, and 46 g of anhydrous potassium dihydrogen phosphate, KH_2PO_4, in distilled water. Dissolve

800 mg of disodium ethylenediamine tetraacetate dihydrate in 100 mL of distilled water. Combine these two solutions and dilute to 1 L with distilled water. Add 20 mg of $HgCl_2$ as a preservative.

5.2 N, N-Diethyl-p-phenylexediamine (DPD) indicator solution - Dissolve 1 g of DPD oxalate or 1.5 g of p-amino-N,N-diethylaniline sulfate in chlorine-free distilled water containing 8 mL of H_2SO_4 (1 + 3) (Section 5.3) and 200 mg of disodium ethylenediamine tetraacetate dihydrate. Dilute to 1 L; store in a colored, glass-stoppered bottle. Discard when discolored. The buffer and indicator sulfate are available as a combined reagent in stable powder form. Caution: The oxalate is toxic; avoid ingestion.

5.3 Sulfuric acid solution (1 + 3) - Slowly add one part of H_2SO_4 (sp gr 1.84) to three parts of distilled water.

5.4 Potassium iodide - KI crystals.

5.5 Stock potassium permanganate solution - Place 0.891 g of $KMnO_4$ in a volumetric flask and dilute to 1 L.

5.6 Standard potassium permanganate solution - Dilute 10.00 mL of stock potassium permanganate solution (Section 5.5) to 100 mL with distilled water in a volumetric flask. One mL of this solution diluted to 100 mL with distilled water is equivalent to 1.00 mg/L Cl.

6.0 CALIBRATION

6.1 Prepare a series of permanganate standards covering the chlorine equivalent range of 0.05 to 4 mg/L.

6.2 Place 5 mL of phosphate buffer in a flask.

6.3 Add 5 mL of DPD reagent.

6.4 Add 100 mL of permanganate standard.

6.5 Read at 515 nm on a spectrophotometer, and record the absorbance.

6.6 Return the contents of the cell to the flask.

6.7 Titrate the contents of the flask with standard ferrous ammonium sulfate (DPD-FAS Method) until the red color is discharged. Record the result.

7.0 PROCEDURE

7.1 Place 0.5 mL of phosphate buffer in a flask.

7.2 Add 0.5 mL of DPD reagent.

7.3 Add approximately 0.1 g of KI.

7.4 Add 10 mL of sample.

7.5 Let stand 2 min.

7.6 Read at 515 nm on a spectrophotometer, and record the absorbance.

8.0 CALCULATIONS

8.1 Calibration Curve Method

8.1.1 Plot the absorbance of the standard permanganate solutions (Section 6.5) on the vertical axis versus the titrated concentration (Section 6.7) on the horizontal axis.

8.1.2 Draw the line of best fit through the points.

8.1.3 Locate the absorbance (Section 7.6) of the sample on the vertical axis.

8.1.4 Read the concentration on the horizontal axis at the intersect of the absorbance and the calibration line.

8.2 Regression Analysis Calculation-Computerized

8.2.1 Enter the absorbance data of the standard permanganate solutions (Section 6.5) and the respective titrated concentrations (Section 6.7) in the appropriate places in the program.

8.2.2 Enter the absorbance data of the sample.

8.2.3 The computer will then display the concentration in mg/L Cl.

9.0 PRECISION AND ACCURACY

9.1 Twenty-five laboratories analyzed prepared samples of 0.66 mg/L Cl. The relative standard deviation was 27.6 percent and the relative error was 15.6 percent.

In a single-laboratory, single-operator situation the following results were obtained.

Sample Matrix	Average (mg/L)	Standard Deviation[a] (± mg/L)	Relative Standard Deviation[a] (Percent)
Distilled Water[a]	0.39	0.012	3.1
	3.61	0.11	3.2
Drinking Water	0.94	0.008	0.8
River Water	0.86	0.02	1.9
Domestic Sewage	1.07	0.03	2.4

a. Three replicates for distilled water. Seven replicates for other samples. For three samples the results were compared to the iodometric titration as a means of obtaining a relative accuracy.

Sample Matrix	Iodometric Titration (mg/L)	DPD Colorimetric (mg/L)	Percent Recovery
Drinking Water	0.86	0.94	109.3
River Water	0.70	0.86	122.9
Domestic Sewage	1.01	1.07	106.0

10.0 REFERENCES

1. Standard Methods for the Examination of Water and Wastewater, 16th Ed., Method 408E, "DPD Colorimetric Method," 1985, p. 309.

2. Bender, D. F. Comparison of Methods for the Determination of Total Available Residual Chlorine in Various Sample Matrices, EPA-600/4-78-019.

RESIDUE, FILTERABLE
(EPA Method 160.1)

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to drinking, surface, and saline waters and domestic and industrial waste.

1.2 The practical range of the determination is 10 mg/L to 20,000 mg/L.

2.0 SUMMARY OF METHOD

2.1 A well-mixed sample is filtered through a standard glass fiber filter. The filtrate is evaporated and dried to constant weight at 180°C.

2.2 If non-filterable residue is being determined, the filtrate from that method may be used for filterable residue.

3.0 INTERFERENCES

3.1 Highly mineralized waters containing significant concentrations of calcium, magnesium, chloride, and sulfate may be hygroscopic and will require prolonged drying, desiccating, and rapid weighing.

3.2 Samples containing high concentrations of bicarbonate will require careful and possibly prolonged drying at 180°C to ensure that all the bicarbonate is converted to carbonate.

3.3 Too much residue in the evaporating dish will crust over and entrap water that will not be driven off during drying. Total residue should be limited to about 200 mg.

4.0 DEFINITIONS

4.1 Filterable residue is defined as those solids capable of passing through a glass fiber filter and dried to constant weight at 180°C.

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

5.1 Preserving the sample is not practical; analysis should begin as soon as possible. Refrigeration or icing to 4°C, to minimize microbiological decomposition of solids, is recommended.

6.0 APPARATUS AND EQUIPMENT

6.1 Glass fiber filter discs - 4.7 cm or 2.1 cm, without organic binder. Reeve Angel type 934-AH, Gelman type A/E, or equivalent.

6.2 Filter holder - Membrane filter funnel or Gooch crucible adapter.

6.3 Suction flask - 500 mL.

6.4 Gooch crucibles - 25 mL (if 2.1-cm filter is used).

6.5 Evaporating dishes, porcelain - 100 mL (Vycor or platinum dishes may be substituted).

6.6 Steam bath.

6.7 Drying oven - 180°C ± 2°C.

6.8 Desiccator.

6.9 Analytical balance - Capable of weighing to 0.1 mg.

7.0 PROCEDURE

7.1 To prepare the glass fiber filter disc, place the disc on the membrane filter apparatus or insert it into the bottom of a suitable Gooch crucible. While a vacuum is applied, wash the disc with three successive 20 mL volumes of distilled water. Remove all traces of water by continuing to apply a vacuum after the water has passed through. Discard washings.

7.2 To prepare evaporating dishes if volatile residue is also to be measured, heat the clean dish to 550 ± 50°C for one hour in a muffle furnace. If only filterable residue is to be measured, heat the clean dish to 180 ± 2°C for one hour. Cool in a desiccator and store until needed. Weigh immediately before use.

7.3 Assemble the filtering apparatus and begin suction. Shake the sample vigorously and rapidly transfer 100 mL to the funnel by means of a 100-mL graduated cylinder. If total filterable residue is low, a larger volume may be filtered.

7.4 Filter the sample through the glass fiber filter, rinse with three 10-mL portions of distilled water and continue to apply vacuum for about 3 min after filtration is complete to remove as much water as possible.

7.5 Transfer 100 mL (or more) of the filtrate to a weighed evaporating dish, and evaporate to dryness on a steam bath.

7.6 Dry the evaporated sample for at least one hour at 180 ± 2°C. Cool in a desiccator and weigh. Repeat the drying cycle until a constant weight is obtained or until weight loss is less than 0.5 mg.

8.0 CALCULATIONS

8.1 Calculate filterable residue using the following equation.

$$\text{Filterable residue (mg/L)} = \frac{(A - B) \times 1,000}{C}$$

where:

A = Weight of dried residue + dish (mg)
B = Weight of dish (mg)
C = Volume of sample used (mL).

9.0 PRECISION AND ACCURACY

9.1 Precision and accuracy are not available at this time.

10.0 REFERENCE

1. Standard Methods for the Examination of Water and Wastewater, 16th Edition, Method 209B, 1985, p. 95.

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RESIDUE, NON-FILTERABLE
(EPA Method 160.2)

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to drinking, surface, and saline waters and domestic and industrial waste.

1.2 The practical range of the determination is 4 mg/L to 20,000 mg/L.

2.0 SUMMARY OF METHOD

2.1 A well-mixed sample is filtered through a glass fiber filter, and the residue retained on the filter is dried to constant weight at 103 to 105°C.

2.2 The filtrate from this method may be used for filterable residues.

[illegible]0 INTERFERENCES

3.1 Filtration apparatus, filter material, pre-washing, post-washing, and drying temperature are specified because these variables have been shown to affect the results.

3.2 Samples high in filterable residue (dissolved solids) (such as saline waters, brines, and some wastes) may be subject to a positive interference. Care must be taken in selecting the filtering apparatus so that washing the filter and any dissolved solids in the filter (Section 7.5) minimizes this potential interference.

4.0 DEFINITIONS

4.1 Non-filterable residue is defined as those solids which are retained by a glass fiber filter and dried to constant weight at 103 to 105°C.

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

5.1 Non-representative particulates such as leaves, sticks, fish, and lumps of fecal matter should be excluded from the sample if it is determined that their inclusion is not desired in the final result.

5.2 Preservation of the sample is not practical; analysis should begin as soon as possible. Refrigeration or icing to 4°C, to minimize microbiological decomposition of solids, is recommended.

6.0 APPARATUS AND EQUIPMENT

6.1 Glass fiber filter discs - Without organic binder, such as Millipore AP-40, Reeves Angel 934-AH, Gelman type A/E, or equivalent.

Note: Because of the physical nature of glass fiber filters, the absolute pore size cannot be controlled or measured. Terms such as pore size collection efficiencies, and effective retention are used to define this property in glass fiber filters. Values for these parameters vary for the filters listed above.

6.2 Filter support - Filtering apparatus with reservoir and a coarse (40 to 60 microns) fritted disc as a filter support.

Note: Many funnel designs are available in glass or porcelain. Some of the most common are Hirsch and Buchner funnels, membrane filter holders, and Gooch crucibles. All are available with a coarse fritted disc.

6.3 Suction flask.

6.4 Drying oven - 103 to 105°C.

6.5 Desiccator.

6.6 Analytical balance - Capable of weighing to 0.1 mg.

7.0 PROCEDURE

7.1 To prepare glass fiber filter disc, place the glass fiber filter on the membrane filter apparatus or insert it into the bottom of a suitable Gooch crucible with the wrinkled surface up. While a vacuum is applied, wash the disc with three successive 20-mL volumes of distilled water. Remove all traces of water by continuing to apply a vacuum after the water has passed through. Remove the filter from membrane filter apparatus or both crucible and filter if Gooch crucible is used, and dry in an oven at 103 to 105 °C for one hour. Remove to a desiccator and store until needed. Repeat the drying cycle until a constant weight is obtained (weight loss is less than 0.5 mg). Weigh immediately before use. After weighing, handle the filter or crucible/filter with forceps or tongs only.

7.2 Selection of sample volume - For a 4.7-cm-diameter filter, filter 100 mL of the sample. If the weight of captured residue is less than 1.0 mg, the sample volume must be increased to provide at least 1.0 mg of residue. If other filter diameters are used, start with a sample volume equal to 7 mL/cm^2 of filter area and collect at least a weight of residue proportional to the 1.0 mg stated above.

Note: If during filtration of this initial volume the filtration rate drops rapidly, or if filtration time exceeds 5 to 10 min, the following scheme is recommended: Use an unweighed glass fiber filter of choice affixed in the filter assembly. Add a known volume of sample to the filter funnel, and record the time elapsed after selected volumes have passed through the filter. Increments of 25 mL are suggested for timing. Continue to record the time and volume increments until the filtration rate drops rapidly. Add additional sample if the filter funnel volume is inadequate to reach a reduced rate. Plot the observed time versus volume filtered. Select the proper filtration volume as that just short of the time a significant change in filtration rate occurred.

7.3 Assemble the filtering apparatus and begin suction. Wet the filter with a small volume of distilled water to seat it against the fritted support.

7.4 Shake the sample vigorously and quantitatively transfer the predetermined sample volume selected in Section 7.2 to the filter using a graduated cylinder. Remove all traces of water by continuing to apply vacuum after sample has passed through.

7.5 With suction on, wash the graduated cylinder, filter, non-filterable residue, and filter funnel wall with three portions of distilled water allowing complete drainage between washing. Remove all traces of water by continuing to apply vacuum after water has passed through.

Note: Total volume of wash water used should equal approximately 2 mL/cm^2. For a 4.7-cm filter, the total volume is 30 mL.

7.6 Carefully remove the filter from the filter support. Alternatively, remove the crucible and filter from crucible adapter. Dry at least one hour at 103 to 105°C. Cool in a desiccator and weigh. Repeat the drying cycle until a constant weight is obtained (weight loss is less than 0.5 mg).

8.0 CALCULATIONS

8.1 Calculate non-filterable residue using the following equation.

$$\text{Non-filterable residue (mg/L)} = \frac{(A - B) \times 1000}{C}$$

where:

A = Weight of filter (or filter and crucible) + residue (mg)
B = Weight of filter (or filter and crucible) (mg)
C = Volume of sample filtered (mL).

9.0 PRECISION AND ACCURACY

9.1 Precision data are not available at this time.

9.2 Accuracy data on actual samples cannot be obtained.

10.0 REFERENCES

1. NCASI Technical Bulletin No. 291, March 1977. National Council of the Paper Industry for Air and Stream Improvement, Inc., 260 Madison Ave., New York, NY.

ANIONS

DETERMINATION OF INORGANIC ANIONS IN AQUEOUS AND SOLID SAMPLES BY ION CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 This method covers the determination of several inorganic anions in aqueous solutions, including chloride (Cl^-), fluoride (F^-), nitrate (NO_3^-), nitrite (NO_2^-), phosphate ($PO_4^=$), and sulfate ($SO_4^=$).

1.2 This is an ion chromatographic (IC) method applicable to the determination of the anions listed above in aqueous samples (e.g., drinking water, surface water, mixed domestic and industrial wastewater) and solid samples (e.g., soils and sediments).

1.3 The method detection limit (MDL) for the above analytes is listed in Table 1. The MDL for a specific matrix may differ from those listed, depending upon the nature of the sample.

1.4 The method should be used by analysts experienced in the use of ion chromatography and in the interpretation of the resulting ion chromatogram. Each analyst must demonstrate the ability to generate acceptable results with this method, using the procedure described in Section 13.2.

1.5 When this method is used to analyze unfamiliar samples for any of the above anions, anion identification should be supported by the addition of spike solutions covering the anions of interest. The spike procedure is described in Section 13.6.4.

2.0 SUMMARY OF METHOD

2.1 A volume of sample is injected into an ion chromatograph. The anions of interest are separated and measured using a system consisting of a guard column, separator column, suppressor column, and conductivity detector. The separator column selectively separates ions according to the affinity of the ions for the resin. The suppressor column converts the eluted ions to acids, which are measured by a conductivity meter. Identification of the ions present is made by retention time. Quantification is accomplished by comparing peak responses of unknown solutions to those of standard solutions.

3.0 INTERFERENCES

3.1 Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution or spiking can be used to solve most interference problems.

3.2 The water dip or negative peak that elutes near and can interfere with the fluoride peak can be eliminated by the addition of the equivalent of 1 mL of concentrated eluent to 100 mL of each standard and sample.

3.3 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms. Specifically, organic contamination will result in a rising baseline.

3.4 Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument columns and flow systems.

3.5 Weak organic acids (formic, acetic, etc.) can coelute with the fluoride and chloride. A weaker eluent is required to eliminate interferences of this type.

3.6 Inorganic ions (I^-, SCN^-, $Cr_2O_7^=$, etc.) that strongly adhere to the column can result in loss of resolution.

4.0 DEFINITIONS

4.1 Stock standard solution - A concentrated solution containing a certified standard that is a method analyte. Stock standard solutions are used to prepare secondary standard solutions.

4.2 Calibration standards - A solution of analytes prepared in the laboratory from secondary standard solutions and diluted as needed to prepare aqueous calibration solutions.

4.3 Quality control check sample - A solution containing known concentrations of analytes, prepared by a laboratory other than the laboratory performing the analysis. The analyzing laboratory uses this solution to demonstrate that it can obtain acceptable identifications and measurements with a method.

4.4 Performance evaluation sample - A solution of method analytes distributed by the EPA's Environmental Monitoring and Support Laboratory in Cincinnati, Ohio (EMSL-Cincinnati), to multiple laboratories for analysis. A volume of the solution is added to a known volume of reagent water and analyzed with procedures used for samples. Results of analyses are used by EMSL-Cincinnati to determine statistically the accuracy and precision that can be expected when a method is performed by a competent analyst. Analyte true values are unknown to the analyst.

4.5 Laboratory control standards - A solution of analytes prepared in the laboratory by adding appropriate volumes of the stock standard solutions to reagent water.

4.6 Laboratory duplicates - Two aliquots of the same sample that are treated exactly the same throughout laboratory analytical procedures. Analyses of laboratory duplicates indicate precision associated with laboratory procedures but not the sample collection, preservation, or storage procedures.

4.7 Field duplicates - Two samples taken at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of field duplicates indicate the precision associated with sample collection, preservation, and storage as well as with laboratory procedures.

4.8 Calibration blank - Calibration solution used to zero instrument response.

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

5.1 Samples should be collected in scrupulously clean glass or polyethylene bottles.

5.2 Aqueous Samples

5.2.1 Sample preservation and holding times for the anions that can be determined by this method are as follows:

Analyte	Preservation	Holding Time
Chloride	None required	28 days
Fluoride	None required	28 days
Nitrate-N	Cool to 4°C	48 hours
Nitrite-N	Cool to 4°C	48 hours
o-Phosphate-P	Filter and cool to 4°C	48 hours
Sulfate	Cool to 4°C	28 days

5.2.2 The method of preservation and the holding time for samples analyzed by this method are determined by the anions of interest. In a given sample, the anion that requires the most preservation treatment and the shortest holding time will determine the preservation treatment and holding time for the total sample. An option is to collect different sample aliquots for different analytes.

5.3 Solid samples collected for the determination of anions should be mixed thoroughly to achieve homogeneity. Solid samples should be preserved by maintaining them at 4°C for and during shipment to the laboratory. Samples must be refrigerated upon receipt at the laboratory until analysis.

6.0 SAFETY

6.1 Normal, accepted laboratory safety practices should be followed during reagent preparation and instrument operations. No known carcinogenic materials are used in this method.

7.0 APPARATUS AND EQUIPMENT

7.1 Balance - Analytical, capable of accurately weighing to the nearest 0.001 g.

7.2 Ion chromatograph - Analytical system complete with ion chromatograph and all required accessories including syringes, analytical columns, compressed air, detector, and stripchart recorder. A data system is recommended for peak integration.

7.2.1 Anion guard column - 4 x 50 mm, Dionex P/N 030825, or equivalent.

7.2.2 Anion separator column - 4 x 250 mm, Dionex P/N 030827, or equivalent.

7.2.3 Anion suppressor column - Fiber, Dionex P/N 35350, or equivalent.

7.2.4 Detector - Conductivity cell, approximately 6-uL volume, Dionex, or equivalent.

7.3 Sample bottles - Glass or polyethylene, of sufficient volume to allow replicate analyses of anions of interest.

7.4 Disposable syringes - Polyethylene.

7.5 Centrifuge tube - Polyethylene, with cap.

7.6 Filters - 0.22 um, disposable.

8.0 REAGENTS

8.1 Reagent water - Distilled or deionized water, free of the anions of interest. Water should contain particles no larger than 0.20 microns.

8.2 Eluent Solutions

8.2.1 Carbonate-bicarbonate eluent (carbonate 0.0024 M, bicarbonate 0.003 M) - Dissolve 1.0176 g of sodium carbonate (Na_2CO_3) and 1.0081 g of sodium bicarbonate in reagent water and dilute to 4 L.

8.2.2 Concentrated carbonate-bicarbonate eluent (carbonate 0.24 M, bicarbonate 0.3 M) - Dissolve 25.45 g of Na_2CO_3 and 25.0 g of $NaHCO_3$ in reagent water and dilute to 1 L.

8.3 Regeneration solution (fiber suppressor) - Sulfuric acid 0.025 N. Dilute 2.8 mL of concentrated sulfuric acid (H_2SO_4) to 4 L with reagent water.

8.4 Stock standard solutions - Stock standard solutions may be purchased as certified solutions or prepared from ACS reagent grade materials (dried at 105°C for 30 min) as listed below.

8.4.1 Chloride (1000 mg/L) - Dissolve 1.6485 g of sodium chloride ($NaCl$) in reagent water and dilute to 1 L.

8.4.2 Fluoride (1000 mg/L) - Dissolve 2.2100 g of sodium fluoride (NaF) in reagent water and dilute to 1 L.

8.4.3 Nitrate (1000 mg/L) - Dissolve 6.0679 g of sodium nitrate ($NaNO_3$) in reagent water and dilute to 1 L.

8.4.4 Nitrite (1000 mg/L) - Dissolve 4.9257 g of sodium nitrite ($NaNO_2$) in reagent water and dilute to 1 L.

8.4.5 Phosphate (1000 mg/L) - Dissolve 4.3937 g of potassium phosphate (KH_2PO_4) in reagent water and dilute to 1 L.

8.4.6 Sulfate (1000 mg/L) - Dissolve 1.8141 g of potassium sulfate (K_2SO_4) in reagent water and dilute to 1 L.

8.4.7 Stock standard solutions are stable for at least one month when stored at 4°C. Dilute working standards should be prepared weekly, except for those that contain nitrite and phosphate which should be prepared fresh daily.

9.0 CALIBRATION

9.1 Establish ion chromatographic operating parameters equivalent to those indicated in Table 1.

9.2 Prepare calibration standards, containing the analyte of interest, at a minimum of three concentration levels and a blank by adding accurately measured volumes of one or more secondary standards (Section 8.4) to a volumetric flask and diluting to volume with reagent water. If the working range exceeds the linear range of the system, a sufficient number of standards must be analyzed to allow an accurate calibration curve to be established. One of the standards should be representative of a concentration near, but above, the method detection limit if the system is operated on an applicable attenuator range. The other standards should correspond to the range of concentrations expected in the sample or should define the working range of the detector. Unless the attenuator range settings are proven to be linear, each setting must be calibrated individually.

9.3 Using injections of 0.05 to 1.0 mL (determined by injection loop volume) of each calibration standard, tabulate peak height or area responses against concentration. The results are used to prepare a calibration curve for each analyte. During this procedure, retention times must be recorded. The retention time is inversely proportional to the concentration.

9.4 The working calibration curve must be verified on each working day, or whenever the anion eluent is changed. If the response or retention time for any analyte varies from the expected values by more than ± 10 percent, new calibration curve must be prepared for that analyte.

9.5 Nonlinear response can result when the separator column capacity is exceeded (overloading). Maximum column loading (all anions) should not exceed about 100 ppm.

10.0 PROCEDURE

10.1 Sample Preparation

10.1.1 Aqueous samples are allowed to come to ambient temperature before analysis and, after thorough mixing, are ready for analysis.

10.1.2 For the determination of extractable anions in solids samples; e.g., soils and sediments, mix the sample thoroughly to achieve homogeneity. For each extraction procedure, weigh (to the nearest 0.001 g) a 0.250-g portion of sample and transfer to a centrifuge tube. Add 20 mL of carbonate-bicarbonate eluent, mix the slurry, and cap the centrifuge tube. Agitate the sample mixture for 1 h at room temperature. Centrifuge the mixture until a clear supernatant is produced. The sample extract is now ready for analysis.

10.2 Table 1 summarizes the recommended operating conditions for the ion chromatograph. Included in this table are estimated retention times that can be achieved by this method. Other columns, chromatographic conditions, or detectors may be used if method detection limits comparable to those listed in Table 1 can be obtained. A laboratory SOP should be written and available to the analyst.

10.3 Calibrate the IC system daily

10.4 Load and inject a fixed amount of well-mixed sample. Flush injection loop thoroughly, using the sample. Use the same size loop for standards and samples. Record the resulting peak size in area or peak height units. An automated constant volume injection system may also be used.

10.5 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for a compound. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

10.6 If the response for the peak exceeds the working range of the system, dilute the sample with an appropriate amount of concentrated carbonate-bicarbonate eluent and re-analyze.

10.7 If the resulting chromatogram fails to produce adequate resolution, or if identification of specific anions is questionable, spike the sample with an appropriate amount of standards and re-analyze.

Note: Retention time is inversely proportional to concentration. Nitrate and sulfate exhibit the greatest amount of change, although all anions are affected to some degree. In some cases, this peak migration can produce poor resolution or misidentification.

11.0 CALCULATIONS

11.1 Prepare separate calibration curves for each anion of interest by plotting peak size in area, or peak height units of standards against concentration values. Compute sample concentration by comparing sample peak response with the standard curve.

11.2 If dilutions were performed, the appropriate factor must be applied to sample values.

11.3 For aqueous samples, report results in mg/L.

11.4 For solid samples a separate determination of percent solids must be performed.

11.4.1 Add a portion of the sample to a tared weighing dish. Weigh and record the weight.

11.4.2 Place weighing dish plus sample, with the cover tipped to allow for moisture escape, in a drying oven that is set at 103 to 105°C. Perform this task in a well-ventilated area.

11.4.3 Dry the sample to constant weight. Cool the sample in a desiccator with the weighing dish cover in place before each weighing. Record each weight. Do not analyze the dried sample.

11.4.4 Calculate and report data on a dry-weight basis. Also report the percent solids for each sample.

$$\text{Percent solids} = \frac{\text{Dry Weight of Sample (g)}}{\text{Wet Weight of Sample (g)}} \times 100$$

11.5 The concentrations determined in the leachate for solid samples are to be reported on the basis of the dry weight of the sample in mg/kg.

$$\text{Concentration (dry wt.) (mg/kg)} = \frac{C \times V}{W \times S}$$

where:

C = Measured concentration (mg/L)
V = Final volume after sample preparation (L)
W = Weight of wet sample (kg)
S = Percent solids/100

12.0 REPORTING

12.1 All reports in the sample data package must be submitted in a legible form.

12.1.1 The data report package for analyses of each sample must be complete before submission and shall include:

12.1.1.1 The Cover Page (see Figure 1) for the IC Anion Analysis Data Package, including DOE and laboratory cross reference numbers, case narrative (comments), and footnotes used in the data package.

12.1.1.2 Tabulated results in mg/L for aqueous samples or mg/kg for solid samples (identification and quantity) of specified chemical constituents (Table 1), validated and signed in original signature by the Laboratory Manager, and reported on Form I (Figure 2). The results for solid samples will be reported on a dry weight basis. Percent solids are not required on aqueous samples. If the value or the result is greater than or equal to the method detection limit (MDL), corrected for dilutions, report the value. All dilutions not required by the contract and affecting the MDL must be noted on an anion-by-anion basis on Form I (see Figure 2). If the value is less than the method detection limits (MDL) in Table 1, put the value in brackets; e.g., [10]. If the anion was analyzed for but not detected, report the instrument detection limit value with a "U" (e.g., 10U).

Note any sample problems in the case narrative. Report results to two significant figures for values from 0 to 100 and three significant figures for results greater than 100. For rounding rules, follow the EPA Handbook of Analytical Quality Control in Water and Wastewater Laboratories (EPA-600d/4-79/019).

12.1.1.3 The spike sample recovery should be reported on Form II (Figure 3). If the spike sample recovery is not within control limits, flag the data with the letter N. An exception to this rule is granted in situations where the sample concentration exceeds the spike concentration by a factor of four or more. In such a case, the spike recovery should not be considered and the data shall be reported unflagged even if the percent recovery does not meet the 85 to 115 percent recovery criteria. In the instance where there is more than one spiked sample per matrix per case, if one spike sample recovery is not within contract criteria, flag all the samples of the same matrix in the case. Individual component percent recoveries (% R) are calculated as follows.

$$\text{Percent recovery} = \frac{(\text{SSR} - \text{SR})}{\text{SA}} \times 100$$

where:

SSR = Spiked sample result
SR = Sample result
SA = Spike added.

12.1.1.4 The duplicate sample analysis should be reported on Form III (Figure 4). If the duplicate sample analysis is not within the control limits, flag it with an asterisk (*). Samples identified as field blanks cannot be used for duplicate sample analysis. The relative percent differences for each component are calculated as follows.

$$RPD = \frac{|D_1 - D_2|}{(D_1 + D_2)/2} \times 100$$

where:

RPD = Relative percent difference
D_1 = First sample value
D_2 = Second sample value (duplicate).

The results of the duplicate sample analysis must be reported on Form III (Figure 4). A control limit of ±10 percent is used for all anions except chloride, which is ±20 percent.

If the duplicate sample results are outside the control limits, flag all the data for samples received associated with that duplicate sample with an asterisk on Forms I and III (Figures 2 and 4). In the instance where there is more than one duplicate sample per case, if one duplicate result is not within contract criteria, flag all the samples of the same matrix in the case.

12.1.1.5 The sample holding times should be reported on Form IV (Figure 5).

13.0 QUALITY ASSURANCE/QUALITY CONTROL

13.1 Each laboratory using this method should have a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability (Section 13.2) and the analysis of spiked samples as a continuing check on performance. The laboratory should maintain performance records to define the quality of data that are generated.

13.1.1 In recognition of the rapid changes occurring in ion chromatography, the analyst is permitted certain options to improve the separations or lower the cost of measurements. Each time such modifications to the method are made, the analyst is required to repeat the procedure in Section 13.2.

13.2 Before performing any analyses, the analyst should demonstrate the ability to generate acceptable accuracy and precision with this method, using a laboratory control standard.

13.2.1 Select a representative spike concentration for each analyte to be measured. Using stock standards, prepare a quality control check sample concentrate in reagent water 100 times more concentrated than the selected concentrations.

13.2.2 Using a pipet, add 1.00 mL of the check sample concentrate (Section 13.2.1) to each of a minimum of four 100-mL aliquots of reagent water. Analyze the aliquots according to the procedure.

13.2.3 Calculate the average percent recovery (R), and the standard deviation(s) of the percent recovery, for the results.

13.2.4 Using the appropriate data from Table 2, determine the single-operator recovery and precision expected for the method, and compare these results to the values calculated in Section 13.2.3. If the data are not comparable within control limits, review potential problem areas and repeat the test.

13.3 The laboratory should develop and maintain separate accuracy statements of laboratory performance for water, wastewater, soils, and sediment samples. An accuracy statement for the method is defined as R ± s. The accuracy statement should be developed by the analyses of four aliquots of each sample solution as described in Section 13.2.2., followed by the calculation of R and s.

13.4 Before processing any samples, the analyst must demonstrate through the analysis of an aliquot of reagent water that all glassware and reagent interferences are under control. Each time there is a change in reagents, a laboratory reagent blank must be processed as a safeguard against laboratory contamination.

13.5 When doubt exists over the identification of a peak in the chromatogram, confirmatory techniques such as sample dilution and spiking must be used.

13.6 Check the instrument standardization by analyzing appropriate quality control check standards as follows:

13.6.1 A quality control sample, preferably an EPA Performance Evaluation Sample for anions, must be used daily for the initial calibration verification. A fresh dilution of this sample shall be analyzed every week thereafter to monitor their stability. If the initial calibration verification solution(s) or performance evaluation samples are not available from EPA, or where a certified solution of an analyte is not available from any source, analyses shall be conducted on an independent standard at a concentration other than that used for calibration, but within the calibration range. An independent standard is defined as a standard composed of the analytes from a different source than those used in the standards for the initial calibration. For IC, the initial calibration verification solution(s) must be run for each anion used in the analysis of the sample. When measurements exceed the control limits of ± 10 percent, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified.

13.6.2 Analyze the calibration blank at a frequency of 10 percent. The result should be within ± 5 times the method detection limits (Table 1). If the result is not within the control level, terminate the analysis, correct the problem and recalibrate the instrument.

13.6.3 For continuing calibration verification, analyze an appropriate instrument check standard containing the anions of interest at a frequency of 10 percent. This check standard is used to determine instrument drift. If agreement is not within ± 10 percent of the expected values, the analysis is out of control. The analysis must be terminated, the problem corrected, the instrument recalibrated, and the preceding 10 samples reanalyzed.

13.6.4 The spiked sample analysis is designed to provide information about the effect of the sample matrix on the digestion in the case of solids and measurement methodology. The spike is added to the solids before the extraction step. At least one spiked sample analysis must be performed on each group of samples of a similar matrix type (i.e., water, soil) and concentration (i.e., low, medium) for each case of samples or for each 20 samples received, whichever is more frequent. Samples identified as field blanks cannot be used for spiked sample analysis.

Table 1. Chromatographic Conditions and Method Detection Limits in Reagent Water

Analyte	Retention Time[a] (min)	Relative Retention Time	Method Detection Limit[b] (mg/L)
Fluoride	1.2	1.0	0.005
Chloride	3.4	2.8	0.015
Nitrite-N	4.5	3.8	0.004
o-Phosphate-P	9.0	7.5	0.061
Nitrate-N	11.3	9.4	0.013
Sulfate	21.4	17.8	0.206

Standard Conditions:

Columns - As specified in Section 7.2
Detector - As specified in Section 7.2
Eluent - As specified in Section 8.2

Sample Loop - 100 uL
Pump Volume - 2.30 mL/min

[a] Concentrations of mixed standard (mg/L)

Fluoride	3.0	o-Phosphate-P	9.0
Chloride	4.0	Nitrate-N	30.0
Nitrite-N	10.0	Sulfate	50.0

[b] MDL calculated from data obtained using an attenuator setting of 1 uMHO full scale. Other settings would produce a MDL proportional to their value.

Table 2. Single-Operator Accuracy and Precision[a]

Analyte	Sample Type	Spike (mg/L)	Number of Replicates	Mean Recovery (%)	Standard Deviation (mg/L)
Chloride	RW[b]	0.050	7	97.7	0.0047
	DW[c]	10.0	7	98.2	0.289
	SW[d]	1.0	7	105.0	0.139
	WW[e]	7.5	7	82.7	0.445
Fluoride	RW	0.24	7	103.1	0.0009
	DW	9.3	7	87.7	0.075
	SW	0.50	7	74.0	0.0038
	WW	1.0	7	92.0	0.011
Nitrate-N	RW	0.10	7	100.9	0.0041
	DW	31.0	7	100.7	0.356
	SW	0.50	7	100.0	0.0058
	WW	4.0	7	94.3	0.058
Nitrite-N	RW	0.10	7	97.7	0.0014
	DW	19.6	7	103.3	0.150
	SW	0.51	7	88.2	0.0053
	WW	0.52	7	100.0	0.018
o-Phosphate-P	RW	0.50	7	100.4	0.019
	DW	45.7	7	102.5	0.386
	SW	0.51	7	94.1	0.020
	WW	4.0	7	97.3	0.04
Sulfate	RW	1.02	7	102.1	0.066
	DW	98.5	7	104.3	1.475
	SW	10.0	7	111.6	0.709
	WW	12.5	7	134.9	0.466

a. Accuracy and precision have not been established for the leachate produced by extraction of the soil and sediment samples.
b. RW = Reagent water.
c. DW = Drinking water.
d. SW = Surface water.
e. WW = Wastewater.

14.0 REFERENCES

1. O'Dell, James W., Pfaff, John D., Gales, Morris E., and McKee, Gerald D., "The Determination of Inorganic Anions in Water By Ion Chromatography," - Method 300.0, EPA-6/4-84-017, March 1984.

2. Handbook for Analytical Quality Control in Water and Wastewater Laboratories, EPA-600/4-79-019.

3. "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020.

4. "OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206 (Revised, January 1976).

5. "Safety in Academic Chemistry Laboratories," American Chemical Society Publications, Committee on Chemical Safety, 3rd Edition, 1979.

6. Clark, Bruce, Private communication, Oak Ridge National Laboratory.

7. "The Determination of Inorganic Anions in Water by Ion Chromatography - Method 300," EPA-600/4-84-017 March, 1984.

8. "Determination of Inorganic Anions in Aqueous and Solid Samples by Ion Chromatography," modified from U.S. EPA Method 300.0 EPA-600/4-84-017 by P.C. Lindahl, Argonne National Laboratory.

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COVER PAGE

DOE Environmental Survey Date ____________

IC ANION ANALYSES DATA PACKAGE

Lab Name ____________
____
Case No. ____________
Q.C. Report No. ____________

Sample Numbers

DOE No.	Lab ID No.	DOE No.	Lab ID No.

Comments: ____________

Footnotes:

NR	- Not required at this time.
Form I:	
Value	- If the result is a value greater than or equal to the instrument detection limit, but less than the required detection limit, report the value in brackets (i.e.; [10]).
U	- Indicates element was analyzed for, but not detected. Report with the method detection limit value (e.g.; 10U]).
E	- Indicates a value estimated or not reported due to the presence of interference. Explanatory note included on cover page.
	- Indicates spike sample recovery is not within control limits.
	- Indicates duplicate analysis is not within control limits.

Figure 1. IC Anion Analyses Data Packages

FORM I

DOE Sample ____________
Date ____________

ANION ANALYSIS DATA SHEET

Lab Name ____________
Case No. ____________
Lab Sample ID No. ____________
Lab Receipt Date ____________
QC Report No. ____________

Elements Identified and Measured

Concentration: Low ________ Medium ________

Matrix Water ________ Soil ________ Sludge ________

Other ________

mg/L or mg/kg dry weight (circle one)

1. Chloride ____________
2. Fluoride ____________
3. Nitrate-N ____________
4. Nitrite-N ____________
5. o-Phosphate-P ____________
6. Sulfate ____________

Percent Solids (%) ____________

Footnotes: For reporting results, standard result qualifiers are used as defined on Cover Page. Additional flags or footnotes explaining results are encouraged. Definition of such flags must be explicit and contained on Cover Page, however.

Comments: ____________

Lab Manager ____________

Figure 2. Anion Analysis Data Sheet

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FORM II
Q.C. Report No. __________
SPIKE SAMPLE RECOVERY

Lab Name ______________________

Date ______________________

Case No. ______________________

DOE Sample No. ______________________

Lab Sample No. ______________________

Units ______________________

Matrix ______________

Anions	Control Limit %R	Spiked Sample Result(SSR)	Sample Result(SR)	Spiked Added(SA)	$\%R^1$
1. Chloride					
2. Fluoride					
3. Nitrate-N					
4. Nitrite-N					
5. o-Phosphate-P					
Sulfate					

$^1\%R = [(SSR - SR)/SA] \times 100$

"N" - out of control

"NR" - Not required.

Comments: ____

Figure 3. Spike Sample Recovery

FORM III
Q.C. Report No. ____________
DUPLICATES

Lab Name ______________________

Date ______________________

Case No. ______________________
DOE Sample No. ______________________
Lab Sample No. ______________________
Units ______________________

Matrix ______________________

Anions	Control Limit[1]	Sample (S)	Dupicates(D)	RPD[2]
1. Chloride				
2. Fluoride				
3. Nitrate-N				
4. Nitrite-N				
5. o-Phosphate-P				
6. Sulfate				

[1] To be added at a later date.

[2] RPD = [S - D/((S + D)/2] x 100

NC - Non calculable RPD due to value(s) less than MDL.

*Out of control.

Figure 4. Duplicates

FORM IV

Q.C. Report No. ________________

HOLDING TIMES

Lab Name ______________________ Case No. ______________

Date __________________________

DOE Sample No.	Matrix	Date Received	Chloride[1] Holding Time (Days)	Fluoride[1] Holding Time (Days)	Nitrate-N[1] Holding Time (Days)	Nitrite-N[1] Holding Time (Days)	O-Phosphate-p[1] Holding Time (Days)	Sulfate[1] Holding Time (Days)

[1] Holding time is defined as the number of days between the date received and the sample analysis date.

Figure 5. Holding Times

HAZARDOUS WASTE CHARACTERISTICS

CORROSIVITY CHARACTERISTIC
(Standard Method 9040)

1.0 SCOPE AND APPLICATION

1.1 This method is used to measure the pH of aqueous waste and that multiphasic waste where the aqueous phase comprises at least 20 percent of the total volume of the waste.

2.0 SUMMARY OF METHOD

2.1 The pH of the sample is determined electrometrically using either a glass electrode in combination with a reference potential or a combination electrode. The measuring device is calibrated using a series of solutions of known pH.

3.0 INTERFERENCES

3.1 The glass electrode, in general, is not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants, or high salinity.

3.2 Sodium error at pH levels greater than 10 can be reduced or eliminated by using a low-sodium-error electrode.

3.3 Coatings of oily material or particulate matter can impair electrode response. These coatings can usually be removed by gentle wiping or detergent washing, followed by distilled water rinsing. An additional treatment with hydrochloric acid (1:9) may be necessary to remove any remaining film.

3.4 Temperature effects on the electrometric determination of pH arise from two sources. The first is caused by the change in electrode output at various temperatures. This interference can be controlled with instruments having temperature compensation or by calibrating the electrode-instrument system at the temperature of the sample. The second source of temperature effects is the change of pH due to changes in the sample as the temperature changes. This error is sample-dependent and cannot be controlled. It should, therefore, be noted by reporting both the pH and temperature at the time of analysis.

4.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

4.1 All samples must be collected using a sample plan that addresses the considerations discussed in this Manual.

4.2 Samples should be analyzed as soon as possible.

5.0 APPARATUS AND EQUIPMENT

5.1 pH meter - Laboratory or field model. A wide variety of instruments are commercially available with various specifications and optional equipment.

5.2 Glass electrode.

5.3 Reference electrode - A silver-silver chloride or other reference electrode of constant potential may be used.

Note: Combination electrodes incorporating both measuring and referenced functions are convenient to use and are available with solid, gel-type filling materials that require minimal maintenance.

5.4 Magnetic stirrer and Teflon-coated stirring bar.

5.5 Thermometer or temperature sensor for automatic compensation.

6.0 REAGENTS

6.1 Primary standard buffer salts are available from the National Bureau of Standards (NBS) and should be used in situations where extreme accuracy is necessary. Preparation of reference solutions from these salts requires some special precautions and handling* such as low-conductivity dilution water, drying ovens, and carbon-dioxide-free purge gas. These solutions should be replaced at least once each month.

6.2 Secondary standard buffers may be prepared from NBS salts or purchased as a solution from commercial vendors. These commercially available solutions have been validated by comparison to NBS standards and are recommended for routine use.

7.0 PROCEDURE

Calibration--Because of the wide variety of pH meters and accessories, detailed operation procedures cannot be incorporated into this method. Each analyst must be acquainted with the operation of each system and familiar with all instrument functions. Special attention to care of the electrodes is recommended.

---

*National Bureau of Standards Special Publication 260.

IGNITABILITY CHARACTERISTIC

(Standard Method 1020)

1.0 SCOPE AND APPLICATION

1.0 This method makes use of the Setaflash Closed Tester to determine the flashpoint of paints, enamels, lacquers, varnishes, and related products and their components that have flashpoints between 0 to 110°C (32 to 230°F) and a viscosity lower than 150 stokes at 25°C (77°F). Tests at higher or lower temperatures are possible.

1.2 The procedure may be used to determine whether a material will or will not flash at a specified temperature or to determine the finite temperature at which a material will flash.

2.0 SUMMARY OF METHOD

2.1 By means of a syringe, 2 mL of sample is introduced through a leakproof entry port into the tightly closed Setaflash Tester or directly into the cup that has been brought to within 3°C (5°F) below the expected flashpoint.

2.2 As a flash/no-flash test, the expected flashpoint temperature may be a specification (e.g., 60°C). For specification testing, the temperature of the apparatus is raised to the precise temperature of the expected flashpoint by slight adjustment of the temperature dial. After 1 min, a test flame is applied inside the cup and note is taken as to whether the test sample flashes or not. If a repeat test is necessary, a fresh sample should be used.

2.3 For a finite flash measurement, the temperature is sequentially increased through the anticipated range, the test flame being applied at 5°C (9°F) intervals until a flash is observed. A repeat determination is then made using a fresh sample, starting the test at the temperature of the last interval before the flashpoint of the material and making tests at increasing 0.5°C (1°F) intervals.

3.0 INTERFERENCES

3.1 Ambient pressure, sample homogeneity, drafts, and operator bias can affect flashpoint values.

4.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

4.1 All samples must be collected employing a sampling plan that addresses the considerations discussed in this Manual.

4.2 The sample size for each test is 2 mL. Obtain at least a 25-mL sample from the bulk source and store in a nearly full, tightly closed clean glass container or in another container suitable for the type of liquid being sampled.

4.3 Erroneously high flashpoints may be obtained if precautions are not taken to avoid loss of volatile materials. Do not open sample containers unnecessarily and do not transfer the sample to the cup unless its temperature is at least 10°C (20°F) below the expected flashpoint. Discard samples in leaky containers.

4.4 Do not use plastic bottles since certain volatile compounds can diffuse through the walls of the bottle.

5.0 APPARATUS AND EQUIPMENT

5.1 Setaflash Tester - As described in Appendix XI of ASTM Method 3278-78.

5.2 Thermometers - Conforming to specifications given in ASTM Method 3278-78. Test to determine that the scale error does not exceed 0.25°C (0.5°F). A magnifying lens significantly assists in making temperature observations.

5.3 Glass syringe - 2 ± 0.1-mL capacity at 25°C (77°F), to provide a means of taking a uniform sample. Check the capacity by discharging water into a weighing bottle and weigh. Adjust plunger if necessary. A disposable syringe of equal precision may be used.

5.4 Cooling block - Aluminum (described in Appendix X2 of ASTM D3278-78), which fits snugly within the test cup for rapid cooling of the sample cup.

5.5 Barometer.

6.0 REAGENTS

6.1 p-Xylene - Reference standard for checking the Setaflash Tester.

6.2 Ice water or dry ice (solid CO_2) and acetone - Cooling mixture.

6.3 Liquified petroleum gas.

6.4 Heat transfer paste.

REACTIVITY CHARACTERISTIC

1.0 SCOPE AND APPLICATION

1.1 The regulation in 40 CFR 261.23 defines reactive waste to include waste having any of the following properties: (1) readily undergoes violent chemical change; (2) reacts violently or forms potentially explosive mixtures with water; (3) generates toxic fumes when mixed with water or, in the case of cyanide or sulfide-bearing waste, when exposed to mild acidic or basic conditions; (4) explodes when subjected to a strong initiating force; (5) explodes at normal temperatures and pressures; or (6) fits within the Department of Transportation's forbidden explosives (Class A, or Class B) classifications.

1.2 This definition is intended to identify waste that, because of its extreme instability and tendency to react violently or explode, poses a problem at all stages of the waste management process. The definition is, to a large extent, a paraphrase of the narrative definition employed by the National Fire Protection Association. The EPA chose to rely on a descriptive, prose definition of reactivity because the available tests for measuring the variegated class of effects embraced by the reactivity definition suffer from a number of deficiencies. For this reason, samples submitted to the lab for evaluation of the reactivity characteristic will be handled on a case-by-case basis. The following definitions, extracted from SW.846, are included for reference.

2.0 DEFINITION

2.1 Characteristic of Reactivity Regulation

A solid waste exhibits the characteristic of reactivity if a representative sample of the waste has any of the following properties.

- It is normally unstable and readily undergoes violent change without detonating.

- It reacts violently with water.

- It forms potentially explosive mixtures with water.

- When mixed with water, it generates toxic gases, vapors, or fumes in a quantity sufficient to present a danger to human health or the environment.

- It is cyanide- or sulfide-bearing, and when exposed to pH conditions between 2 and 12.5, can generate toxic gases, vapors, or fumes in a quantity sufficient to present a danger to human health or the environment.

- It is capable of detonation or explosive reaction if subjected to a strong initiating source or if heated under confinement.

- It is capable of detonation, explosive decomposition, or reaction at standard temperature and pressure.

- It is a forbidden explosive as defined in 49 CFR 173.51, a Class A explosive as defined in 49 CFR 173.53, or a Class B explosive as defined in 49 CFR 173.88.

- It exhibits the characteristic of reactivity, but is not listed as a hazardous waste in Subpart D and has the EPA Hazardous Waste Number of D003.

2.2 Definition of Explosive Materials

For purposes of this regulation, a waste is reactive by reason of explosivity if it meets one or more of the following descriptions.

- It is explosive and ignites spontaneously or undergoes marked decomposition when subjected for 48 consecutive hours to a temperature of 75°C (167°F).

- It is a firecracker, flash cracker, salute, or similar commercial device that produces or is intended to produce an audible effect, the explosive content of which exceeds 12 grains each in weight; pest control bomb, the explosive content of which exceeds 18 grains each in weight; or any such device, without respect to explosive content, which on functioning is liable to project or disperse metal, glass, or brittle plastic fragments.

- It is fireworks combining an explosive and a detonator or blasting cap.

- It is fireworks containing an ammonium salt and a chlorate.

- It is fireworks containing yellow or white phosphorous.

- It is fireworks or firework compositions that ignite spontaneously or undergo marked decomposition when subjected for 48 consecutive hours to a temperature of 75°C (167°F).

- It is a toy torpedo, the maximum outside dimension of which exceeds 7/8 in. or toy torpedo containing a mixture of potassium chlorate, black antimony, and sulfur with an average weight of explosive composition in each torpedo exceeding four grains.

- It is a toy torpedo containing a cap composed of a mixture of red phosphorous and potassium chlorate exceeding an average of one-half grain per cap.

- It is fireworks containing copper sulfate and a chlorate.

- It is an explosive containing an ammonium salt and a chlorate.

- It is liquid nitroglycerin, diethylene glycol dinitrate or other liquid explosives not authorized.

- It is an explosive condemned by the Bureau of Explosives (except properly packed samples for laboratory examinations).

- It is a leaking or damaged package of explosives.

- It is a solid material that can be caused to deflagrate by contact with sparks or flame such as produced by safety fuse or an electric squib, but cannot be detonated (see Note 1) by means of a No. 8 test blasting cap (see Note 2); e.g., black powder or low explosives.

- It is a solid material containing a liquid ingredient and which, when unconfined (see Note 3), can be detonated by means of a No. 8 test blasting cap (see Note 2) or can be exploded in at least 50 percent of the trials in the Bureau of Explosives' Impact Apparatus (see Note 4) under a drop of 4 in. or more, but cannot be exploded in more than 50 percent of the trials under a drop of less than 4 in.; e.g., high explosives or commercial dynamite containing a liquid explosive ingredient.

- It is a solid material containing a liquid ingredient and which, when unconfined, can be detonated by means of No. 8 test blasting cap or can be exploded in at least 50 percent of the trials in the Bureau of Explosives' Impact Apparatus (see Note 4) under a drop of 4 in. or more, but cannot be exploded in more than 50 percent of the trials under a drop of less than 4 in.; e.g., high explosives, or commercial dynamite containing a liquid explosive ingredient, trinitrotoluene, amatol, tetryl, picric acid, ureanitrate, pentolite, or commercial boosters.

- It is a solid material that can be caused to detonate when unconfined by contact with sparks or flame such as produced by safety fuse or an electric squib; or which can be exploded in the Bureau of Explosives' Impact Apparatus in more than 50 percent of the trials under a drop of less than 4 in.;

e.g., initiating and priming explosives, lead azide, fulminate of mercury, or high explosives.

- It is a liquid that can be detonated separately or when absorbed in sterile absorbent cotton by a No. 8 test blasting cap (see Note 2), but which cannot be exploded in the Bureau of Explosives' Impact Apparatus by a drop of less than 10 in. The liquid must not be significantly more volatile than nitroglycerin and must not freeze at temperatures above minus 10°F; e.g., high explosives or desensitized nitroglycerin.

- It is a liquid that can be exploded in the Bureau of Explosives' Impact Apparatus under a drop of less than 10 in.; e.g., nitroglycerin.

- It is a blasting caps (a small tube, usually of an alloy of either copper or aluminum or of molded plastic closed at one end and loaded with a charge of initiating or priming explosives). Blasting caps (see Note 5) that have been provided with a means of firing by an electric current and sealed are known as electric blasting caps.

- It is a detonating primer containing a detonator and an additional charge of explosives, all assembled in a suitable envelope.

- It is a detonating fuse used in the military service to detonate the high-explosive bursting charges of projectiles, mines, bombs, torpedoes, and grenades. In addition to a powerful detonator, detonating fuses may contain several ounces of a high explosive, such as tetryl or dry nitrocellulose, all assembled in a heavy steel envelope. Such fuses may also contain a small amount of radioactive component. Those that will not cause functioning of other fuses, explosives, or explosive devices in the same or adjacent containers are Class C explosives and are not reactive waste.

- It is a shaped charge consisting of a plastic, paper, or other suitable container with a charge not to exceed 8 ounces of high explosive, containing no liquid explosive ingredient, and with a hollowed-out portion (cavity) lined with a rigid material.

- It is ammunition or an explosive projectile, with either fixed, semi-fixed, or separate components, made for use in cannon, mortar, howitzer, recoilless rifle, rocket, or other launching device with a caliber of 20 mm or larger.

- It is a grenade (a small metal or other container designed to be thrown by hand or projected from a rifle). Grenades are filled with an explosive or a liquid, gas, or solid material such as tear gas or an incendiary or smoke-producing material and a bursting charge.

- It is an explosive bomb (metal or other containers filled with explosives). Explosive banks are used in warfare and include airplane bombs and depth bombs.

- It is an explosive mine (metal or composition containers filled with a high explosive).

- It is an explosive torpedo (metal device containing a means of propulsion and a quantity of high explosives).

- It is rocket ammunition (including guided missiles) launched from a tube, launcher, rails, trough, or other launching device, in which the propellant material is a solid propellant explosive. Rocket ammunition consists of an igniter, rocket motor, and projectile (warhead), either fused or unfused, containing high explosives or chemicals.

- It is chemical ammunition (explosive chemical projectiles, shells, bombs, grenades, etc., loaded with tear or other gas, smoke, or incendiary agent). Chemical ammunition also includes cloud-gas cylinders, smoke generators, etc. that may be used to project chemicals.

- o It is a booster, burster, or supplementary charge--Boosters and supplementary charges consist of a casing containing a high explosive and are used to increase the intensity of explosion of the detonator of a detonating fuse. Bursters consist of a casing containing a high explosive and are used to rupture a projectile or bomb to permit release of its contents.
- o It is a jet thrust unit or other rocket motor containing a mixture of chemicals capable of burning rapidly and producing considerable pressure.
- o It is a propellant mixture (i.e., any chemical mixture designed to function by rapid combustion with little or no smoke).

Note 1: The detonation test is performed by placing the sample in an open-ended fiber tube set on the end of a lead block approximately 1-1/2 in. in diameter and 4 in. high which, in turn, is placed on a solid base. A steel plate may be placed between the fiber tube and the lead block.

Note 2: A No. 8 test blasting cap is one containing 2 g of a mixture of 80 percent mercury fulminate and 20 percent potassium chlorate, or a cap of equivalent strength.

Note 3: Unconfined as used in this section does not exclude the use of a paper or soft fiber tube wrapping to facilitate tests.

Note 4: The Bureau of Explosives' Impact Apparatus is a testing device designed so that a guided 8-lb weight may be dropped from a predetermined height to impact specific quantities of liquid or solid materials under fixed conditions. Detailed prints of the apparatus may be obtained from the Bureau of Explosives

(Association of American Railroads, Operations and Maintenance Department, American Railroad Building, Washington, DC 20036; 202-293-4048). The procedures for operating this apparatus are described below.

Method for testing liquids--The anvil is inserted in the receptacle in the anvil housing. A new cup is dropped into the cup-positioning block. One drop of the sample liquid (about 0.01 g) is placed into the cup from a pipet and the cup is revolved until an even film forms on the base. The top striker and the main striker are inserted as far as possible into the upper housing. The upper housing is then placed over the cup-positioning block so that the end of the main striker goes into the brass cup. When the upper housing is removed from the cup-positioning block, the brass cup is picked up on the end of the main striker. When the two housings are screwed together, the brass cup automatically rests firmly on the anvil. An 8-lb weight is dropped from a predetermined height until consistent failure results (a new sample portion and cup are used each time). Flame or flame and noise indicate an explosion, but in either event the brass cup will be belled out or bulged. After making the drop, the weight is raised, the test assembly removed, and the appropriate solvent poured into the top end. The two housings are then separated, the striker removed, and the brass cup removed from the striker end. All solvent is removed carefully and thoroughly before the next drop and the apparatus is cooled and cleaned. The test is repeated, but with a filter-paper disc in the base of the cup under the composition being tested.

Method for testing solids--The die is placed in the anvil assembly, and a small amount of the sample (about 0.01 g)* is placed into the die assembly. The steel striker pellet (plug) and then the striker (plunger) are inserted. The assembly is placed in the apparatus and the drop weight allowed to rest on the striker top to effect even distribution of the explosive. The 8-lb weight is then dropped on the striker from a predetermined height until consistent failure results (i.e., an explosion). A new sample portion is used each time. The die assembly is removed carefully before each test.

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*It is more convenient and safer to devise a small spoon to measure the test sample than to use other methods of measuring the sample.

Note 5: Blasting caps, blasting caps with a safety fuse, or electric blasting caps in quantities of 1,000 or fewer are classified as Class 0 explosives and are not subject to regulation as a reactive waste.

TOXICITY CHARACTERISTIC
LEACHING PROCEDURE

TOXICITY CHARACTERISTIC LEACHING PROCEDURE

1.0 SCOPE AND APPLICATION

1.0 The toxicity characteristic leaching procedure (TCLP) is designed to simulate the leaching a waste will undergo if disposed of in a sanitary landfill. The TCLP is suitable for determining the mobility of both organic and inorganic compounds present in liquid, solid, and multiphasic waste.

1.2 If a total analysis of the waste demonstrates that the individual contaminants are not present or that they are present but at such low concentrations that the appropriate regulatory thresholds could not possibly be exceeded, the TCLP need not be run.

2.0 SUMMARY OF METHOD (See Figure 1)

2.1 For waste containing less than 0.5 percent solids, the waste, after filtration through a 0.6- to 0.8-um glass-fiber filter, is defined as the TCLP extract.

2.2 For waste containing greater than 0.5 percent solids, the liquid phase, if any, is separated from the solid phase and stored for later analysis. The particle size of the solid phase is reduced (if necessary), weighed, and extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. Following extraction, the liquid extract is separated from the solid phase with 0.6- to 0.8-um glass-fiber filter.

2.3 If compatible, the initial liquid phase of the waste is added to the liquid extract and analyzed following filtration. If incompatible, the liquids are analyzed separately and mathematically combined to yield a weighed average concentration.

2.4 Testing of volatile organics with the TCLP is under investigation by the EPA. The present method, as described in FR Vol. 51, No. 114, Friday 13, 1986, is subject to change. This DOE method will reflect those changes as directed by the EPA. Until that time, volatile organics will be excluded from the TCLP.

3.0 INTERFERENCES

3.1 Potential interferences are discussed in the individual analytical methods.

4.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

4.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Section 1 of "Test Methods for Evaluating Solid Wastes" (SW-846).

4.2 Preservatives must not be added to samples.

4.3 Samples can be refrigerated unless refrigeration will result in irreversible physical change to the waste.

4.4 TCLP extracts should be analyzed as soon as possible following extraction. Storage, even for a short period of time, must be at 4°C, and samples for volatiles analysis must not be allowed to come into contact with the atmosphere (i.e., no headspace).

5.0 APPARATUS AND EQUIPMENT

5.1 Agitation apparatus - For this test, an acceptable agitation apparatus (see Table 1) is one capable of rotating the extraction vessel end over end (see Figure 2) at 30 ± 2 rpm.

5.2 Extraction vessel - When the waste is evaluated for other than volatile compounds, an extraction vessel which does not preclude headspace (e.g., a 2-L bottle) is used. Suitable extraction vessels include bottles made from various materials, depending on the constituents to be analyzed and the nature of the waste (Section 5.3.2). These bottles are available from a number of laboratory suppliers. When this type of extraction vessel is used, the filtration device discussed in Section 5.3.2 is used for initial liquid/solid separation and final extract filtration.

5.3 Filtration Devices

5.3.1 Filter holder - When the waste is evaluated for other than volatile compounds, a filter holder capable of supporting a glass-fiber-filter membrane and able to withstand the pressure needed to accomplish separation is used. Suitable filter holders range from simple vacuum units to relatively complex systems capable of exerting pressures up to 50 psi. The type of filter holder used depends on the properties of the material to be filtered. (See Table 2.)

5.3.2 Extraction vessels and filtration devices shall be made of an inert material that will not leach or absorb waste components. Borosilicate glass, polytetrafluoroethylene (PTFE), or Type 316 stainless steel extractors and filter holders must be used when evaluating the mobility of both organic and inorganic components. Plastic devices, such as those made of high-density polyethylene or polypropylene, may only be used when evaluating the mobility of metals.

5.4 Filter Media - Filter media shall be borosilicate glass fiber and have a pore size of 0.6 to 0.8 um, or equivalent. These filters must not contain any binder materials. Filter membranes that meet these properties are identified in Table 3. Pre-filters shall not be used. When evaluating for metals, all filters shall be acid washed prior to use by rinsing with nitric acid (minimum concentration of 1.0 N), followed by three consecutive rinses with deionized distilled water (minimum of 500 mL per rinse).

5.5 pH Meters - Any of the commonly available pH meters are acceptable.

5.6 Laboratory balance - Any laboratory balance accurate to within ± 0.01 g may be used.

6.0 REAGENTS

6.1 Water - ASTM Type 2 deionized distilled water (or equivalent) is used. This water should be monitored periodically for impurities.

6.2 Hydrochloric acid (1.0 N) - ACS Reagent grade.

6.3 Nitric acid (1.0 N) - ACS Reagent grade.

6.4 Sodium hydroxide (1.0 N) - ACS Reagent grade.

6.5 Glacial acetic acid - ACS Reagent grade.

6.6 Extraction Fluid

6.6.1 Extraction Fluid 1 - This fluid is made by combining 64.3 mL of 1.0 N sodium hydroxide and 5.7 mL of glacial acetic acid to the appropriate water (see Section 6.1) and diluting to a volume of 1 L. The pH of this fluid should be 4.93 ± 0.05.

6.6.2 Extraction Fluid 2 - This fluid is made by diluting 5.7 mL of glacial acetic acid with ASTM Type 2 water (see Section 6.1) to a volume of 1 L. The pH of this fluid should be 2.88 ± 0.05.

Note: These extraction fluids should be made up fresh daily. The pH must be checked prior to use to ensure that they are made up accurately. In addition, these fluids should be checked frequently for impurities.

6.7 Analytical standards - Prepared according to the appropriate analytical method.

7.0 PROCEDURE (VOLATILES EXCLUDED)

Although a minimum sample size of 100 g is required, a larger sample size may be necessary depending on the percent solids of the waste sample. It is suggested that enough of the waste sample be collected so that at least 75 g of the solid phase of the waste (as determined using 0.6- to 0.8-um glass-fiber-filter filtration) is extracted. This will ensure that there is adequate extract for the required analyses (e.g., semivolatiles, metals, pesticides, and herbicides).

The extraction fluid to use (see Section 7.12) may also be determined at the start of this procedure. This determination must be on the solid phase of the waste (as determined using glass-fiber-filter filtration).

7.1 If the waste will obviously yield no free liquid when subjected to pressure filtration, weigh out a representative subsample of the waste (100 g minimum) to 0.1 g and proceed to Section 7.11.

7.2 If the sample is liquid or multiphasic, liquid/solid separation using 0.6 to 0.8 um glass-fiber-filter filtration is required. This involves the filtration device discussed in Section 5.3.1, and is outlined in Sections 7.3 to 7.9.

7.3 Pre-weigh the container that will receive the filtrate to 0.1 g. Pre-weigh the filter media to 0.1 g.

7.4 Assemble the filter holder and filter media following the manufacturer's instructions. Place the filter on the support screen and secure. The filter must be acid washed if evaluating for metals.

7.5 Weigh out a representative subsample of the waste (100 g minimum) to 0.1 g. Record the weight of waste sample.

7.6 Allow slurries to stand to permit the solid phase to settle. Waste that settles slowly may be centrifuged prior to filtration.

7.7 Transfer the waste sample to the filter holder.

Note: If the waste material has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Section 7.5 to determine the weight of the waste sample that will be filtered.

Gradually apply a vacuum or gentle pressure of 1 to 10 psi until air or pressurizing gas moves through the membrane. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2-min interval, slowly increase the pressure in 10-psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if no additional liquid has passed through the filter in any 2-min interval, proceed to the next 10 psi increment. When liquid flow has ceased to the point that continued pressure filtration at 50 psi does not result in any additional filtrate within any 2-min period, filtration is stopped.

Note: Instantaneous application of high pressure can degrade glass-fiber filter and may cause premature plugging.

7.8 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase.

Note: Some waste, such as oily waste and some paint waste, will obviously contain material that appears to be a liquid. However, even after applying vacuum or pressure filtration, as outlined in Section 7.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the TCLP extraction as a solid.

7.9 Determine the weight of the liquid phase to 0.1 g by subtracting the weight of the filtrate container (see Section 7.3) from the total weight of the filtrate-filled container. Refrigerate the liquid phase at 4°C and store until time of analysis. The liquid phase of the waste may also be analyzed immediately (refer to Section 7.15). Subtract the weight of the solid phase or the liquid phase from the weight of the total waste sample, as determined in Section 7.5 or 7.7. Record the weight of the liquid and solid phases.

Note: If the weight of the solid phase of the waste is less than 75 g, review the note in Section 7.10.

7.10 The sample will be handled differently from this point, depending on whether it contains more or less than 0.5 percent solids. If the sample obviously has greater than 0.5 percent solids go to Section 7.11. If it appears that the solid may comprise less than 0.5 percent of the total waste, the percent solids will be determined as follows:

7.10.1 Remove the solid phase and filter media from the filtration apparatus.

7.10.2 Dry the filter and solid phase at 100 ± 20°C until two successive weighings yield the same value. Record final weight.

7.10.3 Calculate the percent solids as follows:

$$\text{Percent solids} = \frac{\begin{matrix}\text{Weight of dry} & - \text{ Tared weight} \\ \text{waste and filters} & \text{of filters}\end{matrix}}{\text{Initial weight of waste}} \times 100$$

7.10.4 If the solid comprises less than 0.5 percent of the waste, the solid is discarded and the liquid phase is defined as the TCLP extract. Proceed to Section 7.14.

7.10.5 If the solid is greater than or equal to 0.5 percent of the waste, return to Section 7.1, and begin the procedure with a new sample of waste. Do not extract the solid that has been dried.

Note: This procedure is only used to determine whether the solid must be extracted or whether it may be discarded unextracted. It is not used in calculating the amount of extraction fluid used in extracting the waste nor is the dried solid derived from this step subject to extraction. A new sample will have to be prepared for extraction.

7.11 If the sample has more than 0.5 percent solids, it must now be evaluated for particle size. If the solid material has a surface area per g of material equal to or greater than 3.1 cm^2, or if it is capable of passing through a 9.5-mm (0.375-in.) standard sieve, proceed to Section 7.12. If the surface area is smaller or the particle size is larger than described above, the solid material is prepared for extraction by crushing, cutting, or grinding to a surface area or particle size as described above. When the surface area or particle size has been appropriately altered, proceed to Section 7.12.

7.12 To determine the appropriate extracting fluid to use:

7.12.1 Weigh out a small subsample of the solid phase of the waste, reduce (if necessary) to a particle size approximately 1.0 mm in diameter and transfer a 5.0-g portion to a 500-mL beaker or Erlenmeyer flask.

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7.12.2 Add 96.5 mL of distilled deionized water (ASTM Type 2), cover with watchglass, and stir vigorously for 5 min using a magnetic stirrer. Measure and record the pH. If the pH is <5.0, Extraction Fluid 1 is used. Proceed to Section 7.13.

7.12.3 If the pH from Section 7.12.2 is >5.0, add 3.5 mL 1.0 N HCl, slurry for 30 s, cover with a watchglass, heat to boiling, and simmer for 10 min.

7.12.4 If the pH from Section 7.12.3 is still ≥5 then Extraction Fluid 2 is used.

7.13 Calculate the weight of the remaining solid material by subtracting the weight of the subsample taken in Section 7.12 from the original amount of solid material, obtained in Section 7.1 or 7.9. Transfer the remaining solid material into the extractor vessel, including the filter used to separate the initial liquid from the solid phase.

Note: If any of the solid phase remains adhered to the walls of the filter holder or the container used to transfer the waste, its weight must be determined, subtracted from the weight of the solid phase of the waste, as determined above, and used in calculating the amount of extraction fluid to add to the extractor bottle.

Slowly add an amount of the appropriate extraction fluid (see Section 7.12) to the extractor bottle equal to 20 times the weight of the solid phase that has been placed into the extractor bottle. Close the extractor bottle tightly, secure in rotary extractor device, and rotate at 30 ± rpm for 18 h. The temperature must be maintained at 22 ± 3°C during the extraction period.

Note: As agitation continues, pressure may build up within the extractor bottle (due to the evaluation of gases such as carbon dioxide). To release these pressures, the extractor bottle may be periodically opened and vented to the hood.

7.14 Following the 18-h extraction, the material in the extractor vessel is separated into its component liquid and solid phases by filtering through a new (acid washed if for metals) fiber filter. Follow the directions outlined in Section 7.7.

7.15 The TCLP extract is now prepared as follows:

7.15.1 If the waste contained no initial liquid phase, the filtered liquid material obtained in Section 7.14 is defined as the TCLP extract. Proceed to Section 7.16.

7.15.2 If compatible (i.e., will not form multiple phases), the filtered liquid obtained in Section 7.14 is combined with the initial liquid phase of the waste as outlined in Section 7.9. This combined liquid is defined as the TCLP extract. Proceed to Section 7.16.

7.15.3 If the initial liquid phase of the waste, as obtained in Section 7.9, is not or may not be compatible with the filtered liquid obtained in Section 7.14 (i.e., will form multiple phases), these liquids are not combined. These liquids are collectively defined as the TCLP extract, are analyzed separately, and the results are combined mathematically. Proceed to Section 7.16.

7.16 The TCLP extract will be prepared and analyzed according to the appropriate analytical methods identified elsewhere in this Manual. All TCLP extracts to be analyzed for metals must be acid digested.

Note: If the TCLP extract is multiphasic, the individual phases can be analyzed separately and the results combined mathematically by using a simple weighted average.

$$\text{Final Contaminant Concentration} = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2}$$

where:

V_1 = Volume of the first phase (L)

C_1 = Concentration of the contaminant of concern in the first phase (mg/L)

V_2 = Volume of the second phase (L)

C_2 = Concentration of the contaminant of concern in the second phase (mg/L)

7.17 The constituent concentrations in the TCLP extract are compared to the thresholds identified in the appropriate regulations.

8.0 QUALITY ASSURANCE/QUALITY CONTROL

8.1 All data, including quality assurance data, should be maintained and available for easy reference or inspection.

8.2 A minimum of one blank for every 10 extractions shall be employed as a check to determine if the leaching fluid has been contaminated or if any memory effects from the extraction equipment are occurring. One blank shall also be employed for every new batch of leaching fluid.

8.3 All quality control measures described in the appropriate analytical methods must be followed.

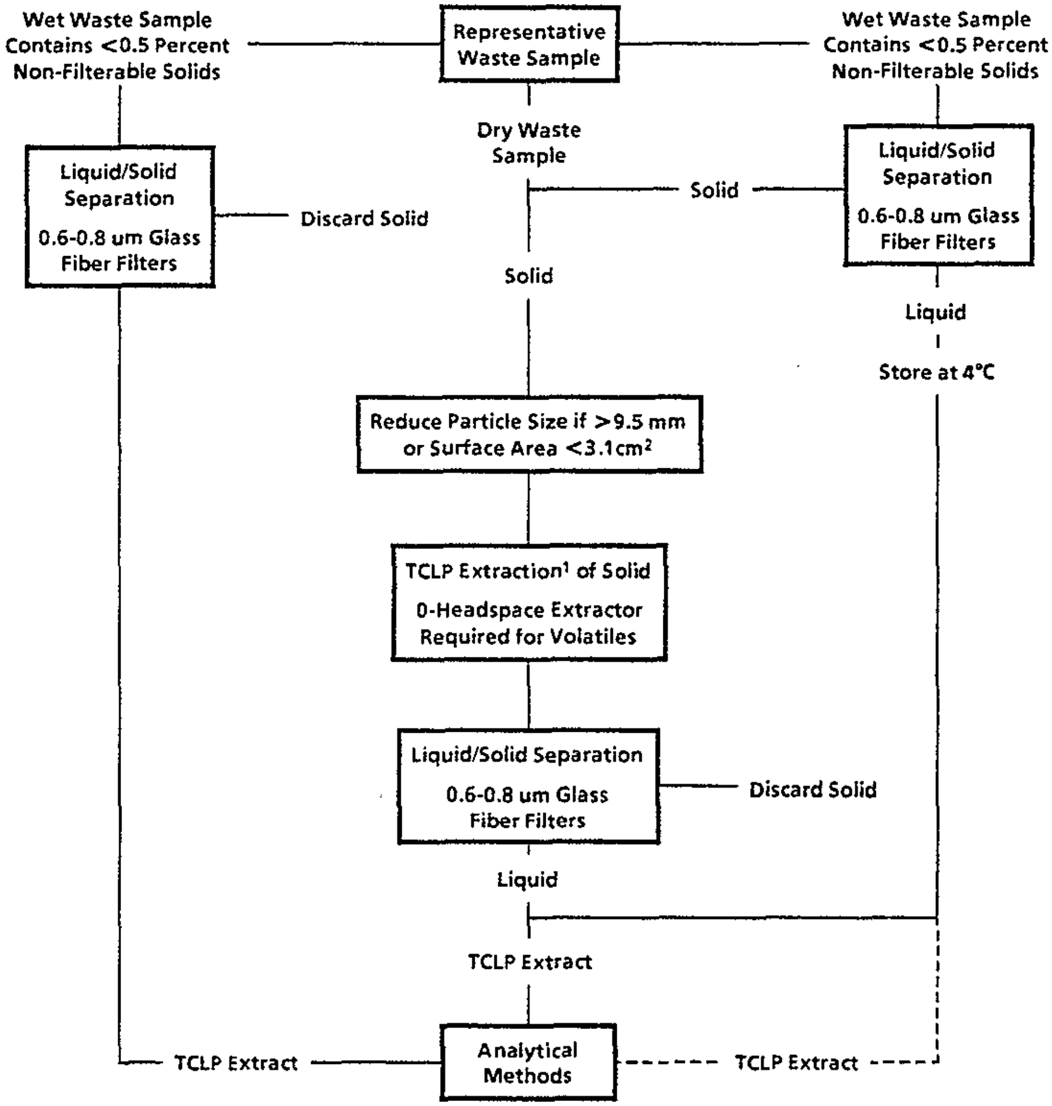
8.4 Stock standard solutions, 1000 mg/L (1 mg/mL)--Stock standard solutions may be purchased as certified solutions or prepared from ACS reagent grade materials (dried at 105°C for 30 min) as listed below.

8.4.1 Chloride (Cl$^-$) 1000 mg/L: Dissolve 1.6485 g sodium chloride NaCl) in reagent water and dilute to 1 L.

8.5 The method of standard addition must be employed for each waste type if (1) recovery of the compound from spiked splits of the TCLP extract is not between 50 and 150 percent, or (2) if the concentration of the constituent measured in the extract is within 20 percent of the appropriate regulatory threshold. If more than one extraction is being run on samples of the same waste, the method of standard addition need only be applied once and the percent recovery applied to the remainder of the extractions.

8.6 TCLP extracts shall be analyzed within the following time periods after generation:

Semivolatiles	40 days
Mercury	28 days
Other Metals	180 days


Wet Waste Sample Contains <0.5 Percent Non-Filterable Solids
Representative Waste Sample
Wet Waste Sample Contains <0.5 Percent Non-Filterable Solids
Dry Waste Sample
Liquid/Solid Separation
0.6-0.8 um Glass Fiber Filters
Discard Solid
Solid
Liquid/Solid Separation
0.6-0.8 um Glass Fiber Filters
Solid
Liquid
Store at 4°C
Reduce Particle Size if >9.5 mm or Surface Area <3.1cm²
TCLP Extraction¹ of Solid
0-Headspace Extractor Required for Volatiles
Liquid/Solid Separation
0.6-0.8 um Glass Fiber Filters
Discard Solid
Liquid
TCLP Extract
TCLP Extract
Analytical Methods
TCLP Extract

[1] The extraction fluid employed is a function of the alkalinity of the solid phase of the waste.

Figure 1. Toxicity Characteristic Leaching Procedure Flowchart

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Billing Code 6560-50-C

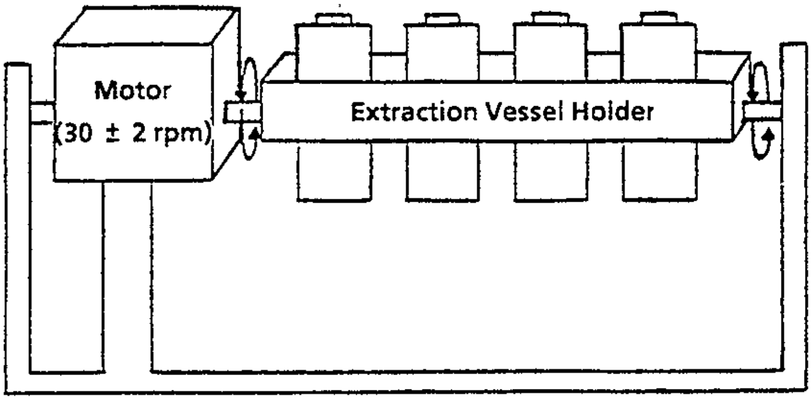
Motor
(30 ± 2 rpm)
Extraction Vessel Holder

Figure 2. Rotary Agitation

Table 1. Suitable Rotary Agitation Apparatus[a]

Company	Location	Model
Associated Design and Manufacturing Company	Alexandria, VA (703)549-5999	4-Hole Device 6-Hole Device
EPRI Extractor		Box Extractor[b]

a. Any device which rotates the extraction vessel in an end-over-end fashion at 30 ± 2 rpm is acceptable.

b. Although this device is acceptable, it is not currently made. It may also require retrofitting to accommodate ZHE devices.

Table 2. Suitable Filter Holders[a]

Company	Location	Model	Size
Nuclepore	Pleasanton, CA (415)463-2350	425900 410400	142 mm 47 mm
Micro Filtration Systems	Dublin, CA (415)828-6010	302300	142 mm
Millipore	Bedford, MA (800)225-3384	YT30142HW XX1004700	142 mm 47 mm

a. Any device capable of separating the liquid from the solid phase of the waste is acceptable, providing that it is chemically compatible with the waste and the constituents to be analyzed. Plastic devices (not listed above) may be used for primarily inoganic waste, when only inorganic constituents are of concern.

Table 3. Suitable Filter Media

Company	Location	Model	Pore Size[a]
Whatman	Clifton, NJ (201)773-5800	GFF	0.7

a. Nominal pore size.

RADIOLOGICAL

DETERMINATION OF ALPHA AND BETA (GROSS ACTIVITY) IN WATER

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to potable water and industrial water which will yield sample residue of less than 5 mg/cm^2 on the counting planchet. The lowest reporting level is 1.0 pCi/L for alpha and 4.0 pCi/L for beta, based on a 500-mL aliquot.

2.0 SUMMARY OF METHOD

2.1 A water is evaporated to a small volume. The concentrated sample is transferred to a counting planchet and dried. The sample is counted independently for gross alpha and gross beta activity.

3.0 INTERFERENCES

3.1 The most serious interference is self-absorption caused by solids on the counting planchet. Thorough discussions of this subject are found in the references (see Section 10.0).

4.0 SAMPLING, PRESERVATION, AND HANDLING

4.1 The samples are collected in new glass bottles, if possible. Use of plastic containers is permissible if it is known that no contaminants are present in the containers.

4.2 Samples may be preserved with nitric acid at a concentration of 2 mL of concentrated HNO_3 per L of sample.

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5.0 APPARATUS AND EQUIPMENT

5.1 Alpha counter.

5.2 Beta counter.

5.3 A combination alpha and beta counter may be used.

5.4 Stainless steel counting dishes (planchets).

6.0 REAGENTS

6.1 Calibration standards - Alpha standards such as ^{238}U and ^{239}Pu are available from the National Bureau of Standards. Beta standards such as ^{137}Cs are also available.

7.0 PROCEDURE

7.1 Transfer an aliquot (100 to 500 mL) of the water sample to a beaker and evaporate it to a small volume on a hot plate. The specified volume of drinking water to be evaporated will be a function of its hardness and solids concentration. Self-absorption factors for the solids present in these volumes have to be determined to correct for losses due to self-absorption. The maximum sample residue should be less than 5 mg/cm^2(2).

7.2 Slurry the residue to a tared stainless-steel planchet, using a rubber policeman and as little water as possible.

7.3 Dry under infrared lamps, cool, weigh, and store in a desiccator.

7.4 The same planchet can be counted for alpha and beta activities in designated instruments, provided their counting chambers are capable of handling the same size planchet.

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7.5 Measure background counts for alpha and beta.

7.6 Count the calibration standards to determine counter efficiency, cpm/dpm (see Section 8.2).

8.0 CALCULATION

8.1 Calculate the concentration of the gross activity (alpha and beta) using the following formula.

$$\text{Gross activity, pCi/liter} = \frac{C \times 10^3}{E \cdot V \cdot W \cdot Y}$$

where:

C = Net count rate (corrected for background) (cpm)

E = Counter efficiency (alpha and beta) (cpm/dpm)

V = Volume of water sample (mL)

W = Self-absorption factor (depending upon solids concentration)

Y = Conversion factor: 2.22 dpm/pCi.

8.2 It is recommended that NBS-calibrated standards be used for ascertaining instrument efficiencies. A weightless deposit of ^{238}U for alpha and a point source from a standard solution of ^{137}Cs for beta are suggested. Standards should also be prepared in the geometry and weight ranges to be encountered in these gross analyses.

8.3 When necessary, the self-absorption factors are applied empirically; this practice depends upon the condition of the sample and the judgment of the analyst. Thorough discussions of the derivation and use of these factors may be found in References 3 and 4.

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9.0 PRECISION AND ACCURACY

9.1 For alpha measurements the precision at the 95 percent confidence level was 20 percent, and recoveries of added alpha activity averaged 85 percent.

9.2 For alpha measurements the precision at the 95 percent confidence level was 15 percent, and there was no bias.

10.0 REFERENCES

1. EPA (U.S. Environmental Protection Agency), March 1976. Interim Radiochemical Methodology for Drinking Water, EPA-600/4-75-008 (Revised).

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3. Shulte, H.F., 1968. Chapter on Monitoring Airborne Radioactivity, Air Pollution, 2nd Edition, Vol. 11, Academic Press; New York.

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DETERMINATION OF ALPHA AND BETA (GROSS ACTIVITY) IN AIR FILTERS

1.0 SCOPE AND APPLICATION

1.1 This method covers the determination of the gross alpha and beta activities in particulates filtered from ambient air.

1.2 Since a given alpha or beta emitter cannot be present at a concentration greater than the gross alpha or beta concentration of a mixture of unidentified radionuclides, a gross analysis (assuming insignificant self-absorption) may eliminate the need for a more time-consuming and expensive analysis for specific radionuclides.

1.3 The method is applicable over the entire range of concentrations of airborne alpha and beta emitters expected to be encountered in the environment.

1.4 A sample of 100 m^3 of air with an alpha particulate concentration of 0.005 pCi/m^3 will contain 1.11 dpm, sufficient to produce acceptable precision with a counting time of less than 1 h in most alpha counters. The lowest concentration of alpha activity reported is 0.005 pCi/m^3. A sample of 100 m^3 of air with a beta particulate concentration of 0.025 pCi/m^3 will contain 5.55 dpm, sufficient to produce acceptable precision with a counting time of 1 h in most beta counters. The lowest concentration of beta activity reported is 0.025 pCi/m^3.

2.0 SUMMARY OF METHOD

2.1 Air particulates collected on a filter paper possessing a high surface retention are counted with alpha and beta sensitive detectors to establish the gross concentration of alpha and beta emitters present in the sampled ambient air.

3.0 INTERFERENCES

3.1 The principal interference is from the progeny of naturally occurring radon and thoron usually present in the atmosphere. Since the effective radioactive half-lives of the progeny of these naturally occurring radionuclides are controlled by relatively short half-life radionuclides (namely 26.8-min ^{214}Pb and 19.7-min ^{214}Bi for radon, and 10.6-h ^{214}Pb for thoron) their interferences may be nullified by waiting until these daughter activities are negligible before counting. This would require about 3 days for the long-lived thoron progeny. Less accurate, but more rapid, evaluations of long-lived gross alpha and beta concentrations can be made using a dual-counting procedure.

3.2 Inert dust loadings on the filter sample may cause serious interference, particularly for measurement of alpha and low-energy beta emitters. Reasonably accurate self-absorption corrections may be made provided these loadings do not exceed a few mg/cm^2 of filter area. Correction factors are determined by measurement of a series of standards of constant specific activity but varying thickness. A graph of apparent activity versus thickness yields a range of correction factors, which are applied by the analyst.

4.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

4.1 Filter samples should be stored so that they are protected from the loss of loosely embedded particles. A properly protected sample should experience no effects other than radioactive decay during storage.

5.0 APPARATUS AND EQUIPMENT

5.1 The basic requirements for gross alpha and beta analysis are an air mover, a calibrated and properly situated device for measuring air-flow rate or sample volume, a particulate filter, an alpha and a beta detector, and counters designed to accommodate the filter samples.

5.2 A windowless or very-thin-window alpha-sensitive detector should be used to count the sample. Solid-state detectors are attractive because of their stability and low background.

5.3 A beta-sensitive detector such as an end-window Geiger-Mueller tube, thin-window proportional flow counter, plastic scintillator, or solid-state detector can be used.

6.0 CALIBRATION

6.1 The efficiency of an alpha or beta counter should be determined with an alpha or beta standard resembling the sample in size and matrix. If the matrix is unknown, an alpha standard may be prepared from a uranium solution and a beta standard may be prepared from a ^{137}Cs solution.

6.2 Determine the background of the counter over an interval similar to or longer than the sample-counting time. Most alpha and beta counters are relatively stable, and it is sufficient to make one daily determination of background to ascertain that major shifts due to malfunction, drift, or contamination have not occurred.

7.0 PROCEDURE

7.1 Operate the air sampler in a location representative of the atmosphere for which the gross alpha and beta concentration is to be determined for a period long enough to collect measurable alpha and beta activity, considering the minimum quantities needed.

7.2 Remove the filter from its holder carefully and place it in a protective cover or container to minimize the possibility of dislodging the collected particulates.

7.3 Place the filter sample in a planchet or holder for reproducible positioning under the detector.

7.4 Count the sample for an interval (or total count) sufficient for a statistically significant result.

8.0 CALCULATIONS

8.1 To calculate the counter efficiency, use the following formula.

$$E = \frac{A}{B}$$

where:

A = Net count rate of standard (cpm)

B = Disintegration rate of standard (dpm).

8.2 To calculate the net sample (alpha or beta) disintegration rate, use the following formula.

$$C\ (\text{dpm}) = \frac{D-F}{E}$$

where:

D = Gross sample counts (cpm)

F = Background counts (cpm).

8.3 To calculate the gross activity (alpha or beta) in air, use the following formula.

$$\text{Activity, pCi/m}^3 = \frac{C}{V \times G}$$

where:

V = Air sample volume (m^3)

G = Conversion factor: 2.22 dpm/pCi.

9.0 PRECISION AND ACCURACY

9.1 The standard deviation (σ) of the count is calculated as follows:

$$\sigma \text{, cpm} = \sqrt{\frac{D}{H} + \frac{F}{I}}$$

$$\sigma \text{, dpm} = \frac{\sigma \text{, cpm}}{E}$$

where:

D, E, and F are as defined in Section 8.0.

H = Sample count time (min)

I = Background count time (min)

9.2 The statistical significance of the count may be expressed as the uncertainty of the count at a specified confidence level, such as 95 percent (1.96).

9.3 A sample of 100 m^3 of air with an alpha particulate concentration of 0.005 pCi/m^3 contains 1.1 dpm. This sample, when counted for 1 h with 50 percent counting efficiency in a counter with a background of 0.20 cpm, will measure 1.10 ±0.48 dpm (at the 95 percent confidence level), which approximates 48 percent RSD.

9.4 A sample of 100 m^3 of air with a beta particulate concentration of 0.025 pCi/m^3 contains 5.55 dpm. This sample, when counted for 1 h at 30 percent counting efficiency in a counter with a background of 1.0 cpm, will measure 5.55 ±1.61 dpm (at the 95 percent confidence level), which approximates 29 percent RSD.

Note: There is no correction in the beta region for the alpha counts.

9.5 The accuracy of a gross alpha and beta analysis is dependent on the accuracy of measurement of the volume of air sampled and the appropriateness of the self-absorption correction (see Section 3.2). Self-absorption corrections are applied in an empirical fashion and depend upon the judgment of the analyst and the condition of the sample. Thorough discussions of the derivation and use of these factors may be found in References 3 and 4.

10.0 REFERENCES

1. Katz, M., (Ed), 1977. Methods of Air Sampling and Analysis, 2nd Edition; Amer. Public Health Assoc., Methods 601 and 602, pp. 630 and 632.

2. Setter, L. R. and G. I. Coats, 1961. "The Determination of Airborne Radioactivity" AIHA J, Vol. 22, p. 64.

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GAMMA SPECTROSCOPY

1.0 SCOPE AND APPLICATION

1.1 The scope of this method includes anything that contains or is a gamma-emitting radionuclide. The method can be applied to soil, water, air filters, etc. providing the sample can be condensed or reduced in size such that it can be placed in a calibrated geometry for counting.

2.0 SUMMARY OF THE METHOD

2.1 A portion (125 g or mL) of the as-received sample is placed in a 125-mL (4-oz) Nalgene wide-mouth bottle to a height of 6.4-cm and weighed. A 10 percent Ge(Li) detector, interfaced with a 4096-channel multichannel analyzer, is used to obtain the gamma spectrum. This spectrum is transferred to a VAX computer, which processes the data using the computer code GAMANAL(1). The GAMANAL program contains gamma-ray libraries and detector efficiencies that permit identification and quantification of gamma-emitting radionuclides. These data are then corrected for room background, self-absorption, and normalization to a dried-weight basis.

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2.2 Soil and sediment samples are typically contained in 500-g glass bottles. Water samples are typically supplied in 1-L plastic bottles. Air filters are usually of cellulose or glass fiber.

2.3 Solid samples are mixed as well as possible in their as-received containers. Liquid samples are shaken immediately before being transferred to the counting container.

2.4 No other sample processing is done except to transfer to a suitable container (or plate) for counting.

3.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

3.1 Place a sticky label of a specified color on a new wide-mouthed 4-oz Nalgene bottle.

3.2 With a laboratory marker, make a line on the bottle at a height of 6.4 cm.

3.3 Zero the top-loading balance. Place a 200-g brass weight, which is stored in a plastic bag to prevent oxidation, on the pan. Record the weight in the logbook for the balance.

3.4 Weigh the empty bottle with cap and label on a top-loading balance with a capacity of 1000 g and sensitivity of 0.001 g. Write this tare weight on the label as "T = XX.XXXg".

3.5 Prepare as many bottles as needed for the sample batch.

3.6 Weigh as many clean, dry 600-mL beakers as needed for the solids in the sample batch. Mark this tare weight on each beaker with a laboratory marker.

3.7 Prepare hood space for sampling procedure by lining hood floor with clean paper towels. These will be discarded and replaced as necessary to keep the outside of the counting bottles clean.

3.8 Arrange samples to be aliquotted in order of date and sample number.

3.9 In the appropriate Survey logbook, record the aliquotting date, analyst(s) preparing aliquot, and the following data from the sample label, when provided: date of sampling at site, time of day of sampling at site in 24-h clock notation, and preservative(s) used, if any.

3.10 With the sample in the hood, and using rubber gloves for protection, open the lid. Note the appearance of the sample and provide a short description in the logbook.

3.11 Place one of the prepared Nalgene bottles and one of the tared 600-mL beakers in the hood. Record the tare weights in the logbook by the number of the sample being aliquotted in the appropriately labelled columns.

3.12 Immediately prior to sampling, mix each sample as well as possible in its as-received condition. Solids are usually stirred with a spatula; liquids are thoroughly shaken to ensure that any solids are in suspension.

3.13 Fill the Nalgene bottle to its marked height of 6.4 cm. Solids should be compacted as well as possible to eliminate channels and air pockets. Replace the lid. The portion of the sample taken for analysis is approximately 25 percent of the total amount of solid sample typically supplied and approximately 5 percent of the liquid sample.

3.14 Wipe the outside of the Nalgene bottle with a clean paper towel and place the sample bottle outside the hood.

3.15 For each solid sample also place a portion of sample in the 600-mL glass beaker. Visually estimate a sample of the approximate size of the sample taken for gamma spectroscopy.

3.16 Weigh the Nalgene bottle and the beaker with the sample aliquots on the top-loading balance. Record the weights in the appropriate "Gross Wt., g" columns by sample number in the logbook.

3.17 With a laboratory marker, draw a circle around "gamma spec" on the original sample bottle label, and write the aliquotting date.

3.18 Remove the sample from the hood and prepare sampling space as needed. Remove any excess sample from spatulas, etc. in the hood by wiping with paper towels and then rinsing and drying before aliquotting another sample.

3.19 Transfer the 600-mL beaker to a drying oven at 110°C. When the sample is dry, remove it from the oven and transfer it to a desiccator to cool. Reweigh the cool beaker containing the dried aliquot on the top-loading balance and record the weight in the logbook.

3.20 Transfer the Nalgene sample bottles to locked cabinet adjacent to the counting room for subsequent analysis.

4.0 APPARATUS AND EQUIPMENT

4.1 Ge(Li) or HPGe detector.

4.2 Spectroscopy amplifier.

4.3 HV bias supply.

4.4 Multichannel analyzer (4096 channels).

4.5 Computer and computer software.

4.6 4-oz wide-mouth Nalgene bottles.

4.7 Aluminum counting plates.

4.8 Top loading balance.

4.9 Drying oven (maintained at 110°C).

5.0 PROCEDURE

5.1 Wrap the 125-mL Nalgene sample bottle in plastic wrap and secure with a rubber band around the neck to prevent possible contamination of the detector.

5.2 Position the sample bottle against the detector face and center it.

Note: On detectors mounted horizontally, set the sample so that the side of the sample bottle touches the detector face and the bottle is centered with respect to the detector. On detectors mounted vertically, set the sample bottle on the detector face so that the bottle is centered.

5.3 Record the count date and the detector number for the appropriate Survey sample number in the logbook.

5.4 Start the count by pressing the Accumulate button on the appropriate multichannel analyzer.

Note: Samples are usually counted for a minimum of 1000 min so that adequate counting statistics can be obtained for the nuclides of interest. Samples with high concentrations of contaminants will require counting times less than this. If the sample-load is light, counting times as long as 1500 min/sample will be used.

5.5 After the gamma spectrum is acquired, store the data on a floppy disk (or magnetic tape) for archival purposes. Then transfer the spectra to the hard disk of the VAX computer system.

5.6 Prepare the data set on the VAX so that the computer program GAMANAL can be used in processing the spectra from the appropriate detector system. The GAMANAL print-out identifies the significant gamma peaks in the spectrum and calculates the disintegration rate of the identified peaks at the time of sampling in the field.

5.7 The disintegration rates of the identified nuclides are next transferred to a sample calculation form where each nuclide is corrected for room background and sample self-absorption and normalized to the dried weight. The corrected nuclide disintegration rates are then converted to pCi/g (or pCi/L) for the final reporting. This calculation is given below.

6.0 CALCULATION

$$\underset{\text{(dried wt.)}}{\text{pCi/g}} = \frac{D \times (C - B) \times SLFABS \times W2}{C \times CF \times SAFS \times W1 \times W3 \times F}$$

where:

D = Disintegrations per min (DPM) at zero time from GAMANAL printout for nuclide of interest

C = Counts per min of nuclide peak of interest

B = Background counts per min of peak of interest

CF = Detector correction factor

SLFABS = Self-absorption factor, standard

SAFS = Self-absorption factor, sample

W1 = As-received weight of sample (g)

W2 = As-received weight of sample aliquot used for determining loss of weight on drying (g)

W3 = Weight of aliquot W2 after drying at 110°C

F = 2.22 DPM/pCi.

7.0 QUALITY CONTROL - QUALITY ASSURANCE

7.1 Accuracy - Efficiency calibration of the Ge(Li) detector(s) is made by counting NBS point-source gamma-emitting nuclides at a source-to-detector distance of 20 cm(2). Secondary standards are prepared using these detector efficiency curves for the calibrated geometry of a 125-mL Nalgene bottle (6.4 cm high by 5.0 cm diameter) containing a soil of a density of approximately one. The propagation of uncertainties in the detector calibrations is estimated to be ±10 percent. Confirmation of the accuracy of the calibrations is demonstrated by counting of radionuclides in NBS SRM 4350B and SRM 4353.

7.2 Precision - The relative standard deviation of a gamma spectroscopy analysis on a soil sample is difficult to assess for a number of reasons. The primary reason is that the samples have a high probability of being nonhomogeneous. For this reason duplicate samples are expected to agree within ±20 percent.

7.3 Quality assurance - Detector efficiency checks and backgrounds are obtained once every week. A ^{137}Cs source is used to ensure that no change in efficiency has occurred during this period. These data are recorded in a bound notebook.

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8.0 REFERENCES

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2. Malewicki, R. L., R. R. Heinrich and R. J. Popek, 1980. "Gamma Spectrometry and Calibration Methods Used in Neutron Dosimetery," Radioelement Analysis: Progress and Problems, Ann Arbor Press, p. 155.

ISOTOPIC COMPOSITION OF URANIUM OR PLUTONIUM

1.0 SCOPE AND APPLICATION

1.1 This procedure involves measuring, by thermal ionization mass spectrometry (TIMS), uranium or plutonium isotope ratios and using these measured ratios for computing the relative abundance of each isotope in a particular sample. It is applicable to any sample from which a sufficient quantity of the element of interest may be isolated in suitably pure form to satisfy the sample-loading requirements of the mass spectrometer employed for the measurements. The procedure presumes that the element of interest has been previously isolated from the sample matrix and is submitted for TIMS analysis in the form of a nitrate salt or in dilute nitric acid solution. Isolation and purification of the element of interest from a given sample matrix may be accomplished by any number of techniques (e.g., solvent extraction or ion-exchange chromatography) depending on the precise nature of the sample matrix. Procedures for carrying out these separation and purification steps are often selected or developed on an ad hoc basis to accommodate the specific chemical composition of a particular sample and are considered not to be within the scope of the present method description.

1.2 Measurements involving the isotopes ^{232}U, ^{238}Pu, and ^{241}Pu may be subject to the effects of isobaric interferences from ^{232}Th, ^{238}U, and ^{241}Am impurities in the sample. For this reason, ^{232}U is not determined in these measurements. In cases where TIMS measurements indicate the presence of significant quantities of ^{238}Pu, the presence of this isotope must be verified by alpha-counting techniques. For measurements involving ^{241}Pu, the plutonium sample must be treated to remove americium and must be analyzed within 48 h of treatment to avoid reappearance of the ^{241}Am product of ^{241}Pu (half-life of 15 years) decay.

2.0 SUMMARY OF METHOD

2.1 Purified samples of the element of interest are received in the TIMS laboratory after being separated from the sample matrix and converted to the nitrate form. Isotopic standards are kept in the laboratory as solutions (1.0 ± 0.1 mg U/mL or 50 ± 10 ug Pu/mL in 0.8 N HNO_3) stored in Teflon bottles.

2.2 Samples in the form of dried nitrate salts are dissolved in 0.8 N HNO_3 to provide a concentration similar to that of the corresponding standards.

2.3 An aliquot of the sample or standard solution containing a prescribed mass of the element to be analyzed is deposited onto an appropriate refractory-metal mass spectrometer filament. For uranium, 1.0 ± 0.2 ug is deposited on a Ta filament; for Pu, 25 to 50 ng is deposited on a Re filament.

2.4 The solution on the filament is evaporated to dryness and oxidized by passing a current through the filament. A programmable dryer is used to control the drying procedure.

2.5 The loaded sample filament is incorporated (together with a second, blank sample filament of the same refractory metal and a rhenium ionizing filament) into a triple-filament ionization assembly for subsequent insertion into the TIMS source.

2.6 Up to 16 ionization assemblies are inserted into the source chamber of a VG Isotopes, Model Isomass 54R, mass spectrometer system.

2.7 The mass-spectrometer source chamber is evacuated and each ionization assembly is, in turn, taken through a filament-degassing sequence.

2.8 Sample identification information is entered into the mass-spectrometer-system computer, appropriate automated-analysis procedures are assigned to each sample in the source chamber, and the automated measurement sequence is initiated.

2.9 Each sample in the source chamber is individually analyzed, under full computer control. The analysis sequence includes (1) setting the temperature of the ionizing filament to provide a prescribed current intensity for Re^+ ions (m/e = 185,187); (2) increasing the temperature of the sample filaments, in a preset manner, until a prescribed total ion current from all isotopes of the element of interest is achieved; (3) measuring, in a prescribed sequence, the ion-current intensity for each individual isotope in the element of interest; and (4) computing and recording the ratio of the ion-current intensity from the peak corresponding to each isotope to that from a designated reference peak. Steps (3) and (4) of the analysis sequence are repeated a prescribed number of times and the individually measured ion-intensity ratios are averaged.

2.10 The average ion-intensity ratios obtained from analysis of the sample are corrected, for bias associated with isotopic fractionation during the analysis, to provide corrected atom ratios of each isotope to the reference isotope. Fractionation corrections are established from analysis of isotopic standard reference materials that are analyzed under the same conditions as the samples.

2.11 Atom-percent abundances of the individual isotopes are computed from the corrected atom ratios. If weight-percent abundances of the isotopes are to be reported, each corrected atom ratio is converted to a corresponding corrected weight ratio by multiplying it by the ratio of nuclidic masses for the isotopes involved. The weight-percent abundances are then computed from the corrected weight-ratio values.

3.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Any appropriate separation and purification methods that will provide suitably pure samples of the element of interest in the form of nitrate salts or in dilute nitric acid solution may be applied. Requirements on the sample preparation procedures include the following.

3.1 The mass of the element submitted for analysis must be sufficient to accommodate the sample-loading requirements of the analysis procedure to be applied. For uranium samples, routine operation requires loading of a nominally 1-ug sample on the mass spectrometer filament, using 10 uL or less of sample solution. For plutonium, the nominal filament loading is 25 to 50 ng from a similar amount of solution. A minimum of 50 uL of solution is considered to be amenable to convenient handling during the loading operations. Thus, a minimum of about 5 ug of uranium or 125 ng of plutonium in the submitted sample is required for measurement by the normal procedure. Smaller amounts of sample may be analyzed, but would require special calibration measurements and would produce results of poorer quality.

3.2 The sample of the given element submitted for analysis must be free of interfering nuclides and chemical impurities that might introduce variations in the mass spectrum background or in the fractionation behavior of the element of interest. In particular, the separation and purification procedures must provide for removal of Am and U from Pu samples in which ^{238}Pu and/or ^{241}Pu are of interest, removal of organic residues from ion-exchange resins or extraction solvents, and removal of all but traces of inorganic components of the sample matrix.

4.0 APPARATUS AND EQUIPMENT

4.1 Thermal ionization mass spectrometer system - V.G. Isotopes, Ltd., Model Isomass 54R; Equipped with Hewlett Packard 9845-B desktop computer, which includes an integral CRT display, integral printer, two integral tape drives, and a floppy disk drive. The mass spectrometer features a 90°-sector, magnetic mass analyzer and deep Faraday-cup detection system.

4.2 Block, sample-mounting - V.G. isotopes.

4.3 Block, filament - NBS-Type.

4.4 Box, sample transfer - A 16-compartment plastic box having compartments labeled in numerical sequence is used.

4.5 Carrier, contact - Available from V.G. Isotopes, Ltd.

4.6 Dryer, Programmable - Fabricated by ANL shops; manual equipment, including a variable current source and a stopwatch, may be substituted.

4.7 Filament, sample - 0.001 in. x 0.030 in. x 0.625 in., Marz-Grade tantalum; 2 required per uranium sample.

4.8 Filament, sample - 0.001 x 0.030 in. x 0.625 in., Zone-Refined rhenium; 2 required per plutonium sample.

4.9 Filament, ionizing - 0.001 in. x 0.030 in. x 0.625 in., zone-refined rhenium.

4.10 Barrel loading record form - See Figure 1.

4.11 Gloves - Lint-free nylon.

4.12 Jig, filament alignment - NBS-Type.

4.13 Jig, sample loading - ANL construction, holds up to 2 filaments for sample deposition.

4.14 Pipet, Gilson Pipetman - 0.1 to 1 mL adjustable volume, with disposable plastic tips.

4.15 Socket, filament transfer - 2 required, labeled "1" and "2".

4.16 Rod, Pyrex - 6 mm x 16 mm, reusable.

4.17 Syringe - Micro Scientific Glass Engineering Model 5TT, 5-uL capacity with disposable Teflon tips.

4.18 Tools - Including pliers, screwdrivers, tweezers, spline wrenches, etc.

4.19 Workstation - Environmental Air Control Model LAB-1, exhausting, Class 100 clean air; 2 required.

5.0 REAGENTS

5.1 Nitric acid solution - 0.8 N HNO_3, prepared from NBS-distilled nitric acid and laboratory distilled, demineralized water.

5.2 Plutonium isotopic reference materials - New Brunswick Laboratory Certified Reference Material 128 (primarily ^{239}Pu and ^{242}Pu in certified ratio of approximately 1:1); 50 ± 10 ug Pu per mL in 0.8 N HNO_3, stored in Teflon bottles.

5.3 Uranium isotopic reference materials - National Bureau of Standards Reference Materials from Series U-002 through U-970 (primarily ^{235}U and ^{238}U in certified ratios ranging from 1:200 to 200:1); 1.0 ± 0.1 mg U per mL in 0.8 N HNO_3, stored in Teflon bottles.

6.0 CALIBRATION

6.1 Calibration of the mass spectrometric isotope ratio determinations is equivalent to establishing a value for the constant E_o in Section 8.1. Our system uses a value for E_o which is determined as the running average of values from the 10 most recent standard runs that precede the sample run. The validity of this calibration is tested each time an additional standard run is performed by computing results for the standard at hand using the calibration factor determined from the 10 previous standard runs. Calibration is considered verified if the ratio of principal isotopes in the standard falls within the 99 percent confidence interval about its certified value. For runs with the uranium SRMs, this interval extends to ±0.15 percent of the certified value. In the case of plutonium standards, the interval corresponds to a difference of ±0.3 percent, relative to the certified value. If the result obtained for a given standard falls outside the limits for acceptance, additional standard runs are performed to determine whether the calibration actually shifted or whether the discrepant result reflected a legitimate value from the tails of the probability distribution. If a shift in calibration is encountered, the reason for the shift is identified and dealt with before the system is recalibrated so that analyses may proceed.

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6.2 The standards that are run before and after each group of samples for the purpose of evaluating each isotopic blank (see Section 10.2) serve also in calibrating and verifying calibration of the system. If either of these standard runs provides evidence of a calibration shift and such a shift is verified by running additional standards, then all of the unknown samples in the group shall be re-analyzed after the system has been recalibrated.

7.0 PROCEDURE

7.1 Loading Sample on Mass Spectrometer Filament

Note: Because labeling of individual loaded filaments and ionization assemblies is impractical, provision is made in the procedure to minimize potential for confusion among samples and to record sample identification in terms of the location of the filament on which the sample is loaded. These objectives are accomplished in the following way.

a. Samples are stored in a hood separate from the workstations in which filaments are loaded and mounted in ionization assemblies.

b. Only one sample container at a time is permitted in the filament-loading workstation. This sample is loaded on a filament located in one of the two positions in the workstation. The positions are used in numerical sequence and are recorded for each sample on a Barrel Loading Record form (see Figure 1).

c. Loaded filaments are transferred, in sockets numbered to correspond to the loading-workstation positions, to the assembly workstations. The filaments are mounted one at a time, again in numerical sequence, into ionization assemblies.

d. Each assembly is placed directly into a numbered compartment in a sample transfer box keeping the same sequence as established on the Barrel Loading Record.

7.1.1 Sample Loading Procedure

7.1.1.1 Attach the sample Barrel Loading Record form to the clipboard adjacent to the filament-loading workstation. Record the date, your initials, and any appropriate comments on the form.

7.1.1.2 Select the sample to be loaded from those in the sample storage area. Transfer the sample to the filament-loading workstation. (Note: Only one sample container is permitted in the workstation at any time).

7.1.1.3 Write the sample identification number in the first available line on the Barrel Loading Record form.

7.1.1.4 If the sample to be loaded is in the proper solution form (1.0 ± 0.2 mg U/mL or 50 ± 25 ug Pu/mL in 0.8 N HNO_3, proceed to Section 7.1.1.6.

7.1.1.5 If the uranium sample is in the form of a dried nitrate salt, dissolve the sample as follows:

  7.1.1.5.1 Affix a clean, unused plastic tip to the Pipetman pipet.

  7.1.1.5.2 Using the pipet, dispense a volume of 0.8 N HNO_3 into the sample beaker to give a concentration of 1 mg U/mL solution for uranium samples or 25 to 50 ug Pu/mL for plutonium samples.

  7.1.1.5.3 Swirl the solution gently to dissolve the sample.

  7.1.1.5.4 Discard the pipet tip.

7.1.1.6 Insert two tantalum (uranium samples) or rhenium (plutonium samples) sample filaments in the sample-loading jig (one filament if only a single sample is to be loaded). Tighten the holding screws.

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7.1.1.7 Switch the programmable sample dryer to AUTO and press RESET to ensure that no voltage will be applied to the filaments when the filament leads are connected.

7.1.1.8 Connect the electrical leads to the filament loading posts. If only a single filament is being loaded, install a shorting clip in the second connector.

7.1.1.9 Place a clean, unused Teflon tip on the microsyringe.

7.1.1.10 Using the microsyringe, transfer 1 uL of the sample solution (1 ug U or 25 to 50 ng Pu) to the central portion of the first unused filament in the sample-loading jig. If the solution wets the filament and spreads beyond one-half the filament length, discard the filament to the appropriate waste container and replace it with another according to the steps in Sections 7.1.1.6 through 7.1.1.8. Then repeat the sample addition.

7.1.1.11 Discard the syringe tip to the appropriate radioactive waste container.

7.1.1.12 Replace the Parafilm cover on the sample beaker and return the beaker to the sample storage hood.

7.1.1.13 If a second filament is to be loaded with sample, repeat the steps in Sections 7.1.1.2 through 7.1.1.12 for this sample.

7.1.1.14 When satisfactory addition of solution on the filament(s) is achieved, press START on the programmable sample dryer. The drying sequence is as follows:

0.5 A, 10 min
1.0 A, 1 min
1.5 A, 1 min
1.8 A, 1 min
Total Time: 13 min

The dryer emits an audible signal when the drying cycle is complete.

7.1.1.15 After the drying cycle is ended, inspect the sample deposit on each filament. To be acceptable, the deposit must be a thin, adherent coating located in the central 1/3 to 1/2 of the sample filament. If these criteria are not met, discard the filament to the appropriate radioactive waste container and reload the sample following the steps in Sections 7.1.1.2 through 7.1.1.14.

7.1.1.16 Disconnect the electrical leads from the filament posts.

7.1.1.17 Select the filament transfer socket labeled "1" and attach it to the posts of the filament in the "1" position of the filament-loading jig.

7.1.1.18 Loosen the holding screws on this position and, using the transfer socket to hold the filament, transfer the loaded filament to the assembly workstation.

7.1.1.19 Using the filament transfer socket labeled "2," repeat the steps in Sections 7.1.1.17 and 7.1.1.18

for the filament in position "2" of the sample-loading jig.

Note: If more samples remain to be loaded, up to two of these may be carried through the steps in Sections 7.1.1.2 through 7.1.1.16 at this point. Mounting of the already-loaded filaments into individual ionization assemblies (Section 7.1.1.2) would then proceed during the drying cycle of Section 7.1.1.14. Mounting operations on the already-loaded filaments must be completed before the step in Section 7.1.1.17 is performed on the newly loaded ones.

7.1.1.20 Wearing lint-free Nylon gloves, select the filament in transfer socket "1."

7.1.1.21 Mount the loaded filament into an NBS-Type filament block together with a rhenium ionizing filament and a blank sample filament of the same type as the loaded filament. Tighten all holding screws securely.

7.1.1.22 Insert the filament block into the alignment jig and align the filaments by bending the support posts as needed.

7.1.1.23 Remove the filament block from the alignment jig, insert the block into a V.G. Isotopes sample mounting block, and attach a contact-carrier plate.

7.1.1.24 Insert a 6-mm glass-rod spacer between the filament posts.

7.1.1.25 Inspect the completed ionization assembly and adjust if necessary to make sure that the ionizing filament is aligned in the center of the exit slit and that none of the contact carrier wires are touching each other.

7.1.1.26 Place the assembly in the next available compartment in the sample transfer box. Verify that this number corresponds to the number indicated on the Barrel Loading Record for this sample.

7.1.1.27 Repeat the steps in Sections 7.1.1.21 through 7.1.1.26 for the filament in transfer socket "2."

7.1.1.28 If additional samples remain to be loaded, proceed to 7.1.1.2 or 7.1.1.15 as appropriate.

7.1.1.29 When all designated samples have been processed, attach the Barrel Loading Record form to the cover of the sample transfer box, and move the box to the mass spectrometer for insertion of the ionization assemblies into the source.

7.2 Source-Chamber Venting, Sample Insertion, and Re-evacuation

7.2.1 Verify that analyses of previously loaded samples have been completed and that the instrument is in the idle state.

7.2.2 Close the analyzer isolation valve, tightening until the scribed marks on the valve housing are aligned.

7.2.3 Set accelerating voltage power supply output to ZERO and switch off power to the unit.

7.2.4 Set ion-gauge control to OFF.

7.2.5 Connect a supply of low-pressure (<5 psig), dry nitrogen to the source-chamber vent valve.

7.2.6 Close the mechanical-pump isolation valve.

7.2.7 Close the electrometer-head evacuation valve.

7.2.8 Verify that each of the above steps has been completed.

7.2.9 Switch off the turbomolecular pump. The source chamber will vent automatically after a 1 to 2 min delay.

7.2.10 As the chamber is venting, loosen the four retaining nuts on the two source-chamber flanges, but do not remove the nuts.

7.2.11 When the source chamber reaches atmospheric pressure as indicated by release of the flanges, disconnect the dry-nitrogen supply and close the supply valve.

7.2.12 Remove the flange-retaining nuts, then the flanges. Place the flanges vacuum-side-up on an adjacent table.

7.2.13 Using a clean 6-in. screwdriver, loosen the retaining screws of each spent sample assembly.

7.2.14 Remove the electrical connection to the barrel-drive motor. This allows the barrel to be turned manually during removal and insertion of sample assemblies.

7.2.15 Wearing lint-free gloves, remove the spent samples as follows:

  7.2.15.1 Rotate the barrel until the filament assembly to be removed is positioned adjacent to the side source-housing port.

7.2.15.2 Remove the assembly and place it in the tray designated for spent sample assemblies.

7.2.15.3 Proceed in this manner until all spent sample assemblies have been removed.

7.2.16 Insert each fresh sample assembly into the barrel-loading position (1 through 16 as stamped on the barrel) that corresponds to the sample assembly position in the sample transfer box and as indicated on the "Isomass 54R Barrel Loading Record" form (see Figure 1) completed during filament loading.

7.2.17 When all fresh sample assemblies have been inserted, tighten the retaining screws of each assembly.

7.2.18 Manually rotate the barrel through all loaded positions to verify that the barrel turns freely.

7.2.19 Replace the source-housing flanges, install the flange retaining nuts and, using fingers only, tighten the nuts.

7.2.20 Open the mechanical-pump valve.

7.2.21 Start the turbomolecular pump.

7.2.22 When the backing-line pressure reaches 50 mbar (approximately 2 min), open the electrometer head evacuation valve.

7.2.23 Switch on the ion gauge. Pressure after 3 to 4 min of pumping should be 10^{-5} mbar or less.

7.2.24 Switch on the accelerating voltage supply, but leave it in the standby mode.

7.2.25 Allow the system to pump down to a pressure of 10^{-6} mbar or less (takes 15 to 30 min). Then proceed to Section 7.3.

7.3 Sample Degassing

Note: For procedural steps that involve input through the computer keyboard, text enclosed in brackets is to be entered exactly as written; EXECUTE, RUN, and CONT refer to specific keys on the keyboard.

7.3.1 Verify that the source chamber pressure is less than 10^{-6} mbar.

7.3.2 Insert the electrical connector into the barrel drive-motor socket.

7.3.3 Switch on the filament current supply.

7.3.4 Switch the accelerating voltage supply from "standby" to "on" and set the output to 1 kV.

7.3.5 Switch on the computer and the disk-drive unit.

7.3.6 When the message 9845B READY FOR USE appears on the CRT screen, type [MASS STORAGE IS ":F8"] and press EXECUTE.

7.3.7 Type [GET "PREHET"] and press EXECUTE.

7.3.8 When loading of the program has been completed, as indicated by the absence of the run light in the lower righthand side of the screen, press RUN.

7.3.9 Following computer prompts, input positions (as numbers from the series 1 through 16) which are to be degassed.

Note: When the above information is entered, each filament assembly in turn will be rotated into position and degassed at a preset current level (4.5 A for ionizing filament, 1.5 A for side filaments) under computer control. Required time is approximately 3 min per sample position.

7.3.10 When the degassing of all indicated sample positions is complete (the message DEGASSING COMPLETED displayed by the computer), fill the source-chamber cold trap with liquid nitrogen and proceed to Section 7.4.

7.4 Initiation of Measurement Sequence

7.4.1 Type [GET "MEASUR"] and press EXECUTE.

7.4.2 Ensure that the printer paper supply is sufficient for the number of analyses that will be performed.

7.4.3 When the program is loaded, as indicated by the absence of the run light, press "RUN."

7.4.4 Set all instrument controls to the Auto position, marked with red arrows.

7.4.5 Set the chart recorder to the 100-mV range.

7.4.6 Verify that the electrical connection to the barrel drive motor is in place.

7.4.7 Open the analyzer isolation valve.

7.4.8 Following computer prompts, indicate the amount of printout desired for the samples being run (usually printout level "2") and select the appropriate measurement procedure for each of the 16 positions that contain samples.

7.4.8.1 For uranium samples or standards, specify the procedure designated "U-238 Ref, with 233." This procedure employs a center-filament temperature corresponding to a rhenium ion current of 1×10^{-12} A, and a measurement sequence in which the uranium ion current is increased in stages. The measurement sequence at each stage is divided into runs and cycles. For each run, the uranium peaks are centered and focused. For each cycle within a run, peak and background signals are measured in a prescribed sequence and the peak-intensity ratio relative to the reference isotope is computed for each isotope other than the reference. The individual ratios are printed in hardcopy as the analysis proceeds. The analysis sequence is as follows:

Stage	Uranium Ion Current, A	Runs	Cycles
1	1×10^{-11}	1	3
2	2×10^{-11}	1	3
3	3×10^{-11}	1	3
4	3×10^{-11}	3	12

The first three stages permit the ion currents to stabilize and, although ratios are measured and recorded, are not intended to provide useful data. The 12 ratios recorded for each isotope in each run of the fourth stage are averaged and their standard deviation is estimated. Outliers are automatically evaluated and rejected as appropriate. Upon completion of the third run of the fourth stage, the 36 ratios from the three fourth-stage runs are treated together to provide a grand-average ratio value and an estimated standard deviation of the mean of the measured values. The computer program that controls the uranium analysis procedure automatically applies fractionation corrections to each grand average ratio based on the 10 most recent standard runs stored on disk, converts the corrected atom ratios to weight ratios, and computes atom- and weight-percent abundances of the uranium isotopes of mass 233, 234, 235, 236, and 238 (see Section 8.0 for a description of calculations). If the sample is identified as a uranium isotopic standard, the uncorrected ratios are automatically stored in the appropriate file on disk for use in computing the appropriate fractionation correction for subsequent runs. Results of the statistical treatment and isotope-abundance calculations are provided as part of the printout that forms the raw-data record of each mass spectrometric analysis.

7.4.8.2 For plutonium samples or standards, specify the procedure designated "PLUT, General, 239 Ref, 0.5 V." This procedure operates in a manner similar to that of the uranium procedure described above, and provides ion-intensity ratios for Pu isotopes of mass 238, 240, 241, 242, and 244 relative Pu-239. The measurement sequence employs a Re ion current of 2 x 10^{-12} A and the following pertinent sample-analysis specifications:

Stage	Plutonium Ion Current, A	Runs	Cycles
1	1.7 x 10^{-12}	1	3
2	3.4 x 10^{-12}	1	3
3	5 x 10^{-12}	1	3
4	5 x 10^{-12}	3	10

Data records provided by this program are similar to those from the uranium analysis except that 238/239 ratios are not averaged or treated statistically, and the program does not apply fractionation corrections to the measured ion-intensity ratios. The corrections must be separately applied and the isotopic abundances must be separately calculated as described in Section 8.0.

7.4.9 When all loaded positions are assigned, press Special Function Key (SFK) No. 7 to indicate completion of this setup phase.

7.4.10 Following computer prompts, input sample identification numbers given on the Barrel Loading Record form.

Note: Input of the last sample number completes the setup of the system. The analysis sequence begins immediately and continues until all samples have been analyzed or until the sequence is stopped by the operator.

8.0 CALCULATIONS

8.1 Determination and Application of Fractionation Corrections

Isotopic fractionation in the mass spectrometer causes the observed ion-intensity ratios to differ from the true atom ratios in the sample by a factor whose magnitude depends on the conditions of analysis and the masses of the isotopes involved in the ratio. For uranium and plutonium isotopes, the true ratio may be obtained from the corresponding ion-intensity ratio by application of a correction factor, $C_{i/j}$, given in the following formula.

$$C_{i/j} = 1 + \frac{i - j}{3} \cdot E_o$$

where i and j represent the mass numbers of the isotopes involved in the ratio in question and E_o is a constant determined from measurements performed under identical conditions on isotopic standard reference materials whose major isotopes differ in mass number by three units. This corresponds to the 235/238 pair in available NBS uranium standards or the 239/242 pair in the CRM 128 plutonium standard. Different values for E_o apply to the different elements.

The magnitude of E_o for a given element is evaluated using the relationship:

$$1 + E_o = \frac{R_{cert}}{R_{meas}}$$

where R_{cert} is the certified value of the appropriate (235/238 for uranium, 239/242 for plutonium) atom ratio in the reference material, and R_{meas} is the value obtained for the corresponding grand-average ion-intensity ratio from analysis of the standard. The corrected atom ratio of isotope i to isotope j in each sample is computed from the observed ratio, R_{obs}, and the relationship

$$R_{i/j,corr} = C_{i/j} \cdot R_{obs}$$

8.2 Calculation of Corrected Weight Ratios

The corrected weight ratio, ${}^{W}R_{i/j,corr}$, of isotope i to isotope j is computed as the product of the corrected atom ratio and the ratio of nuclidic masses, m, of the isotopes.

$$ {}^{W}R_{i/j,corr} = R_{i/j,corr} \cdot m_i/m_j $$

Values for the nuclidic masses are:

Uranium Nuclide	Isotope Mass	Plutonium Nuclide	Isotope Mass
233	233.039	238	238.0496
234	234.041	239	239.0522
235	235.044	240	240.0538
236	236.046	241	241.0568
238	238.051	242	242.0587
		244	244.0642

8.3 Calculation of Isotopic Abundances

The percent relative atom abundance, A_i, of each isotope, i, in a mixture of isotopes is computed from the corrected isotope ratios and the relationship

$$ A_i = \frac{R_{i/r,corr} \times 100\%}{\sum_j R_{j/r,corr}} $$

where $R_{i/r,corr}$ is the corrected atom ratio of isotope i to the reference r, and the summation in the denominator is taken over all isotopes in the mixture, including i and r. Note that, by definition, the ratio $R_{r/r,corr}$ is unity.

Percent relative weight abundance, W_i, of the individual isotopes in a mixture is computed from a relationship identical to the previous equation, except that corrected weight ratios rather than corrected atom ratios are employed:

$$W_i = \frac{{}^{W}R_{i/r,corr} \times 100\%}{\sum_j {}^{W}R_{j/r,corr}}$$

9.0 REPORTING

Results of the mass spectrometric determinations of isotopic abundances are reported on a standard Report of Chemical Analysis Form [No. CMT-84 (10-84)]. Unless otherwise requested, results are reported both as atom percent abundances and as weight percent abundances. Each isotopic abundance is assigned an individual estimate of uncertainty corresponding to an interval half-width equal to at least twice the standard deviation of the reported abundance, as estimated using a treatment based on the discussion in Section 11.0.

10.0 QUALITY ASSURANCE/QUALITY CONTROL

10.1 The presence of isotopic impurities in the reagents and materials used in the mass spectrometric procedure will introduce a positive error in the measured isotope ratios if the impurity isotopes are different from the reference isotope. Experience has shown that levels of isotopic impurities which affect the uranium and plutonium analyses may be kept at negligible levels by selecting high-quality filament materials and reagents and by following the sample-handling precautions that have been incorporated into this procedure. The absence of isotopic impurities in the filament materials and reagents is demonstrated by analyzing nearly monoisotopic samples of the elements of interest and obtaining ratios for the minor isotopes (relative to the major isotope), which conform to the expected isotopic composition of the sample material.

10.1.1 For uranium analyses, a natural uranium sample (NBS950a) is used to demonstrate the absence of impurities affecting all isotopes except ^{238}U. This latter isotope is evaluated by analysis of NSB SRM 993, which is highly enriched in ^{235}U and has a certified ^{238}U content. Alternatively, a highly enriched sample of ^{233}U may be used to evaluate the blank levels of all isotopes other than ^{233}U, and the blank levels of ^{233}U may be assessed by analysis of the $^{238}U/^{235}U$ isotopic SRMs from NBS.

10.1.2 For plutonium analyses, CRM 996 from the New Brunswick Laboratory offers the means to evaluate blank levels of all Pu isotopes except ^{244}Pu. Since this latter isotope is not present in CRM 128 at significant levels, calibration and calibration-verification runs with this CRM serve to confirm the absence ^{244}Pu in the procedure blank.

10.2 Each group of uranium or plutonium samples analyzed by mass spectrometry shall be bracketed by measurements on the appropriate reference materials to ensure that blank levels of each isotope are negligible. For uranium, one NBS SRM and one ^{233}U sample shall be run before and after each group of no more than 20 unknown uranium samples. For plutonium, one sample of CRM 128 and one sample of CRM 996 shall be run before and after each group of no more than 20 unknown plutonium samples. If a significant blank is observed for any isotope, as evidenced by a corrected ratio larger than the expected value by 1×10^{-5}, absolute, then the source of the blank shall be determined and eliminated and the unknown samples will be re-analyzed.

[illegible].0 PRECISION AND ACCURACY

11.1 The corrected isotope ratios used in computing the isotopic abundance values for any given sample are virtually free of bias relative to the isotopic reference materials employed for the system calibration. The absence of bias in the corrected ratio has been demonstrated using data obtained from measurements in which the standard materials were analyzed as unknowns. One set of 96 analyses of NBS SRM U-500, performed over the time period from December 1982 through October 1985, showed an average value for the ratio of principal isotopes, which differed from the certified ratio by only 0.005 percent, relative. Similarly extensive data are not presently available for the CRM 128 plutonium standard, but because the bias-correction procedure is completely analogous, residual bias in the corrected ratios is anticipated to also be negligibly small.

11.2 The standard deviation of an individual measurement of a given isotope ratio involves a within-run component that arises from signal noise in the mass spectrometer measuring systems or from minor instabilities in the ion beam and a between-run component that reflects variations in sample purity, sample loading, and instrument operating conditions from one run to the next. The within-run component is estimated for each ratio of each sample by the computer program that calculates the average ratio values, using the data from replicate ratio measurements performed during the run. The between-run component is estimated from replicate analyses of a particular sample or standard. Typically, the within-run variations show a standard deviation of a few (2 to 3) ppm, absolute, in the average measured ratio and are relatively independent of the masses involved. The between-run component, on the other hand, is proportional to the magnitude of the ratio and to the difference between the masses involved. Based on replicate analyses of standards, the between-run standard deviation for a single measurement of a uranium isotope ratio where the masses differ by 3 units is 0.05 percent, relative. A corresponding value for plutonium is 0.1 percent, relative.

For each isotope ratio measured for a given sample, the standard deviation of the ratio may be calculated from the following expression.

$$\sigma^2(R_{i/j}) = \sigma^2_{\text{within},i/j} + \left[\frac{i - j}{3} \cdot R_{i/j} \cdot \sigma_{\text{between},3}\right]^2$$

where $\sigma\,(R_{i/j})$ stands for the standard deviation of the given ratio, $\sigma_{\text{within},i/j}$ is the standard deviation of the average ratio measured during the run for the specified pair of isotopes, and $\sigma_{\text{between},3}$ is the between-run standard deviation estimated from replicate measurements on a standard which has principal isotopes that differ by 3 mass units. For small ratio values (0.001 or less), precision is limited by the measuring systems and the within-run component dominates in determining the standard deviation of the ratio. For larger ratio values, the between-run component increases in importance and ultimately determines the magnitude of the standard deviation when $R_{i/j}$ is greater than about 0.1.

When the set of isotope ratios measured for a given sample is used with the equation in Section 8.3 for calculating the atom- or weight-percent abundance of each isotope in the sample, the standard deviation of each abundance value may be estimated from the standard deviations of the individual ratios by the method of error propagation, using the following or an analogous equation involving weight ratios.

$$\sigma^2(A_i) = A_r^2.[(1 - 2f_i) \quad \sigma^2(R_{i/r}) + f_i^2. \; \Sigma\, \sigma^2(R_{j/r})]$$

Here, the notation   (X) represents the standard deviation of the variable X, the subscript r represents the reference isotope in the ratios, the f_i are given by $A_i/100$ percent, and the summation is taken over all measured ratios. This expression shows that the standard deviation of the isotope abundances depends not only on the magnitude of the measured ratios, but also on the specific isotopic composition of the sample being analyzed. In general, the precision for abundance determinations is greatest for samples that are highly enriched in a single isotope. The standard deviation of the abundance of the principal isotope in such cases is smaller than 0.001 percent. When the principal isotope in a given sample has an abundance approaching 50 percent, the corresponding standard deviation may be as large as 0.03 percent, depending on the exact distribution of other isotopes in the sample.

ISOMASS 54R BARREL LOADING RECORD

Date__________

Position No.	Dryer Pos.	Sample Number	Int. Std.	Comments
1				
2				
3				
4				
5				
6				
7				
8				
9				
10				
11				
12				
13				
14				
15				
16				

Figure 1. Barrel Loading Record Form

DETERMINATION OF PLUTONIUM ISOTOPES IN WATER

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the determination of plutonium in potable, natural, and industrial waters.

1.2 At Oak Ridge National Laboratory (ORNL), the lowest concentration reported is 4×10^{-5} pCi/mL when analyzing a 1-L sample, using 10 dpm of plutonium-242 tracer, counting for 1000 min on an alpha pulse-height analyzer system with a detector having a 20 percent efficiency and a 0.005-cpm background over each energy region of interest, and realizing an 80 percent chemical recovery of the plutonium.

1.3 At other plants, the lowest reported concentration is 1×10^{-3} pCi/mL for 1-L samples.

2.0 SUMMARY OF METHOD

2.1 The plutonium in the sample is equilibrated with plutonium-242 tracer, coprecipitated with bismuth phosphate, adsorbed on anion exchange resin, selectively eluted from the resin, coprecipitated with praseodymium hydroxide, and extracted with thenoyltrifluoroacetone-xylene. The plutonium extract is dried on a stainless-steel disc which is analyzed by alpha pulse-height analysis to determine the plutonium concentrations.

3.0 INTERFERENCES

3.1 Interferences from other alpha-emitting nuclides are generally eliminated by alpha pulse-height analysis, except for ^{240}Pu which cannot be resolved from ^{239}Pu by this means. Mass spectrometric analysis is required if independent measurements of both of these isotopes are desired.

4.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

4.1 If suspended and/or soluble plutonium determinations are desired, the samples should first be filtered to remove the suspended particulates as soon as practicable; then the samples should immediately be adjusted to 3 M with nitric acid.

4.2 If total plutonium determinations are desired, the samples should be adjusted to 3 M with nitric acid as soon as practicable without filtering.

4.3 After preliminary treatment, the samples are stored in either glass or plastic containers.

5.0 APPARATUS AND EQUIPMENT

5.1 Glass ion-exchange column - 8-mm I.D. by 25-cm long, fitted with a stopcock and reservoir.

5.2 Hot plate.

5.3 Centrifuge.

5.4 Vortex mixer.

5.5 Extraction vials - 50 mL with plastic-lined caps.

5.6 Lab glassware.

5.6.1 Beakers - To accommodate sample aliquot, and 250-mL size.

5.6.2 Centrifuge tubes - 50-mL glass and 100-mL glass and plastic.

5.7 Transfer pipets.

5.8 Stainless steel counting discs.

5.9 Multichannel analyzer system with silicon surface-barrier detector(s).

6.0 REAGENTS

6.1 Nitric acid - Concentrated.

6.2 Nitric acid (8 M) - Add 500 mL of concentrated HNO_3 to 500 mL of water.

6.3 Bismuth nitrate solution (0.1 M) - Dissolve 20.9 g of bismuth metal in nitric acid and dilute to 1 L with 8 M HNO_3.

6.4 Phosphoric acid - Concentrated.

6.5 Ammonium hydroxide - Concentrated.

6.6 Plutonium-242 tracer - Dilute an NBS-certified (or equivalent) solution of ^{242}Pu to a concentration of 10 dpm per mL with 2 M HNO_3 and store in glass.

6.7 Nitric acid (2 M) - Add 125 mL of concentrated HNO_3 to 500 mL of water and dilute to 1 L with water.

6.8 Nitric acid (1 M) - Dilute 2 M HNO_3 1:1 with water.

6.9 Sodium nitrite - $NaNO_2$ crystals.

6.10 Sodium nitrite solution (3 M) - Dissolve 10.4 g of sodium nitrite ($NaNO_2$) in water and dilute to 50 mL with water. Make fresh daily.

6.11 Hydrochloric acid (8 M) - Add 666 mL of concentrated HCl to 334 mL of water.

6.12 Thenoyltrifluoroacetone (TTA) - Xylene solution. 0.5 M TTA - Dissolve 111 g of $SC_4H_3COCH_2COCF_3$ (TTA) in xylene and dilute to 1 L with xylene.

6.13 Ferric nitrate solution (0.1 M) - Dissolve 40.4 g of ferric nitrate nonahydrate [$Fe(NO_3)_3 \cdot 9H_2O$] in water and dilute to 1 L with water.

6.14 Hydroxylamine hydrochloride solution (5 M) - Dissolve 347.5 g of hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) in water and dilute to 1 L with water.

6.15 Hydrochloric acid-hydroxylamine hydrochloride solution (0.5 M) HCl-0.05 M $NH_2OH \cdot HCl$ - Add 42 mL of concentrated HCl and 10 mL of 5 M NH_2OH-HCl to 500 mL of water and dilute to 1 L with water.

6.16 Praseodymium carrier solution - Dissolve 12.82 g of praseodymium nitrate dihydrate [$Pr(NO_3)_3 \cdot 2H_2O$] in 500 mL of water and dilute to 1 L with water.

6.17 Anion exchange resin - Dowex 1-X4 (50 to 100 mesh, chloride form) or equivalent.

7.0 PROCEDURE

7.1 Transfer a measured aliquot of the sample to an adequate-sized beaker and adjust the acidity to 0.1 M with concentrated HNO_3.

7.2 Add 1 mL of 10 dpm/mL ^{242}Pu tracer solution.

7.3 Add 1.25 mL of 0.1 M bismuth solution per L of sample.

7.4 Add 1 gram of $NaNO_2$ crystals per L of sample.

7.5 Place on a hot plate and digest the sample solution at 70°C for two hours with stirring.

7.6 Add 5.25 mL of concentrated H_3PO_4 per L of sample, remove from heat, and stir frequently for one hour.

7.7 Allow the $BiPO_4$ precipitate to settle overnight.

7.8 Without disturbing the precipitate, withdraw and discard the supernatant liquid.

7.9 Transfer the precipitate to a 100-mL glass centrifuge tube, centrifuge at 2000 rpm for 10 min, and discard the supernatant solution.

7.10 Transfer the precipitate to a 250 mL beaker with 25 mL of concentrated HNO_3 and heat to dissolve the precipitate.

7.11 Add an equal volume of water to adjust the acidity to 8 M.

7.12 Add 2 mL of 3 M $NaNO_2$ solution and heat to boiling.

7.13 Allow the sample to digest for 20 min to adjust the valence of the plutonium to Pu^{+4}.

7.14 While the sample is digesting, prepare a resin column as follows.

7.14.1 Place a glass-wool plug in the bottom of the column described in Section 5.1.

7.14.2 Slurry the resin (see Section 6.17) with water and immediately discard the fines by decanting. Repeat as necessary until fines are removed.

7.14.3 Transfer 4 mL of resin to the column with water. Prevent any channeling by maintaining the solution level above the resin by use of the stopcock.

7.14.4 Place a glass-wool plug on top of the resin.

7.14.5 Convert the resin to the nitrate form by passing several column volumes of 8 M HNO_3 through the column until the resin is free of chloride ions.

7.15 Transfer the sample solution, which should be at room temperature, to the prepared resin column, and allow it to flow through the column at a rate of 2 mL per min. Discard the effluent solution.

7.16 Rinse the beaker with 25 mL of 8 M HNO_3 and transfer the rinse to the column. Allow the 8 M HNO_3 rinse to flow through the column at a rate of 2 mL per min. Discard the effluent solution.

7.17 Rinse the beaker with 25 mL of 8 M HCl and transfer the rinse to the column. Allow the 8 M HCl rinse to flow through the column at a rate of 2 mL per min. Discard the effluent solution.

7.18 Add one drop of 0.1 M $Fe(NO_3)_3$ and 1 mL of 5 M $NH_2OH \cdot HCl$ to the column. Open the stopcock and allow the solution to drain to the top of the resin bed, then stop the flow. Discard the effluent solution.

7.19 Add 4 mL of 0.5 M HCl-0.05 M $NH_2OH \cdot HCl$ solution. Place a 50 mL glass centrifuge tube under the column. Allow 3 mL of solution to drain into the tube and close the stopcock.

7.20 Allow 20 min digestion time for reduction of the plutonium to Pu^{+3}.

7.21 Add 25 mL of 0.5 M $NH_2OH \cdot HCl$ solution. Pass the solution through the column at a flow rate of 2 mL per min into the 50-mL tube.

7.22 Add 1 mL of praseodymium carrier to the sample solution in the 50-mL tube and mix thoroughly.

9 2 1 2 4 5 7 1 2 3 6

7.23 Add concentrated NH_4OH with stirring to a pH of 9.0. Allow 15 min digestion time.

7.24 Centrifuge for 10 min at 1500 rpm and discard the supernatant solution.

7.25 Wash the precipitate with water, centrifuge, and discard the water wash solution.

7.26 Dissolve the precipitate in 6 drops of concentrated HNO_3 and transfer the dissolved sample to a 50-mL extraction vial with 5 mL of 1 M HNO_3. Add 10 drops of 3 M $NaNO_2$, mix well, and allow 20 min digestion time for plutonium to oxidize to Pu^{+4}.

7.27 Add 1 mL of 0.5 M TTA-xylene solution and extract on a Vortex mixer for 10 min.

7.28 Centrifuge for 2 min to separate the phases. Discard the aqueous phase.

7.29 Scrub the TTA extract with 5 mL of 1 M HNO_3. Centrifuge and discard the aqueous phase.

7.30 Transfer the TTA to a stainless-steel disc placed on a hot plate. Set at 150°C. Allow the TTA to dry thoroughly.

7.31 Flame the stainless-steel disc to a red heat.

7.32 Measure the alpha activities by pulse height analysis with a silicon surface-barrier detector coupled to a multichannel analyzer.

8.0 CALCULATIONS

$$^{238}\text{Pu, pCi/mL} = A \cdot K \cdot C / D \cdot E$$
$$^{239}\text{Pu, pCi/mL} = B \cdot K \cdot C / D \cdot E$$

where:

A = Net integrated counts of ^{238}Pu from pulse analysis

B = Net integrated counts of ^{239}Pu from pulse analysis

C = dpm of ^{242}Pu added

D = Net integrated counts of ^{242}Pu from pulse analysis

E = Volume of sample, mL

K = Conversion factor to pCi = 1 pCi/2.22 dpm.

9.0 PRECISION AND ACCURACY

9.1 The precision is estimated to be ±20 percent.

9.2 The accuracy has not been established.

10.0 REFERENCES

1. Johns, Frederick B., (Ed), February 1975. Handbook of Radiochemical Analytical Methods, EPA-680/4-75-001.

2. Coleman, George H., September 1, 1965. "The Radiochemistry of Plutonium," National Academy of Sciences - National Research Council, NAS-NS 3058.

DETERMINATION OF PLUTONIUM ISOTOPES IN AIR FILTERS

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the determination of plutonium-238 and -239 in filter paper and Hollingsworth types of air filters.

1.2 At Oak Ridge National Laboratory (ORNL), the lowest concentration reported is 0.04 pCi/total filter sample, using 10 dpm of plutonium-242 tracer, counting for 1000 min on an alpha pulse-height analyzer with a detector having a 20 percent efficiency and a 0.055-cpm background over each energy region of interest, and realizing an 80 percent chemical recovery of the plutonium. Typically, for filters that have filtered 1×10^{3} cubic m of air, the lowest concentration reported then is 4×10^{-5} pCi/m.

1.3 At other plants, the lowest concentration reported is 0.1 pCi/total filter sample.

2.0 SUMMARY OF METHOD

2.1 Plutonium-242 tracer is added to the dissolved-filter solution, and valence-adjustment steps are taken to equilibrate the tracer with the sample plutonium. After being adjusted to Pu^{+4}, Pu is adsorbed on ion-exchange resin, reduced to Pu^{+3}, and selectively eluted from the resin. Subsequently, plutonium is carried on praseodymium hydroxide, dissolved and oxidized to Pu^{+4}, which is then extracted with thenoyltrifluoroacetone-xylene. The organic extract is evaporated on a stainless steel disc, and the plutonium is determined by alpha spectrometry.

3.0 INTERFERENCES

3.1 Plutonium-240 cannot be distinguished from plutonium-239 by alpha pulse-height analysis. However, alpha pulse-height analysis eliminates most other alpha interferences.

4.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

4.1 Filters should be handled as little as possible to avoid loss of particulates and should be stored in plastic containers, such as polyethylene bags.

5.0 APPARATUS AND EQUIPMENT

5.1 Analytical balance.

5.2 Muffle furnace - Capable of maintaining a temperature of 525°C.

5.3 Hot plate.

5.4 Centrifuge.

5.5 Vortex mixer.

5.6 Extraction vials - 50 mL, with plastic-lined screw caps.

5.7 Teflon beakers - 250 mL.

5.8 Transfer pipets.

5.9 Lab glassware

5.9.1 Beakers - 100 mL, 250 mL, and 500 mL.

5.9.2 Centrifuge tubes - 50 mL, glass.

5.9.3 Glass ion-exchange column - 8-mm I.D. by 25-cm long, fitted with a stopcock and reservoir.

5.10 Stainless steel counting discs.

5.11 Multichannel analyzer system with silicon surface-barrier detector(s).

6.0 REAGENTS

6.1 Nitric acid - Concentrated.

6.2 Nitric acid (8 M) - Add 500 mL of concentrated HNO_3 to 500 mL of water.

6.3 Ammonium hydroxide - Concentrated.

6.4 Plutonium-242 tracer solution - Dilute an NBS-certified (or equivalent) solution of ^{242}Pu to a concentration of 10 dpm per mL with 2 M HNO_3 and store in glass.

6.5 Nitric acid (1 M) - Add 62.5 mL of concentrated HNO_3 to 300 mL of water and dilute to 1 L.

6.6 Sodium nitrite - $NaNO_2$ crystals.

6.7 Sodium nitrite solution (3 M) - Dissolve 10.4 g of sodium nitrite ($NaNO_2$) in water and dilute to 50 mL. Make fresh daily.

6.8 Thenoyltrifluoroacetone (TTA)-xylene solution, 0.5 M TTA - Dissolve 111 g of $SC_4H_3COCH_2COCF_3$ (TTA) in xylene and dilute to 1 L with xylene.

6.9 Ferric nitrate solution (0.1 M) - Dissolve 40.4 g of ferric nitrate nonahydrate [$Fe(NO_3)_3 \cdot 9H_2O$] in water and dilute to 1 L.

6.10 Hydroxylamine-hydrochloride solution (5 M) - Dissolve 347.5 g of hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) in water and dilute to 1 L.

6.11 Hydrochloric acid-hydroxylamine hydrochloride solution (0.5 M HCl-0.5 M NH_2OH-HCl) - Add 42 mL of concentrated HCl and 10 mL of 5 M NH_2OH-HCl to 500 mL of water and dilute to 1 L.

6.12 Hydrochloric acid - Concentrated.

6.13 Praseodymium carrier solution - Dissolve 12.82 g of praseodymium nitrate dihydrate [$Pr(NO_3)_3 \cdot 2H_2O$)] in 500 mL of water and dilute to 1 L with water.

6.14 Anion exchange resin - Dowex 1-X4 (50-100 mesh, chloride form) or equivalent.

6.15 Hydrochloric acid (8 M) - Add 666 mL of concentrated HCl to 334 mL of water.

6.16 Hydrogen peroxide - 30 percent solution.

6.17 Hydrofluoric acid - Concentrated.

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7.0 PROCEDURE

7.1 Carefully place the filter sample in an adequate-size beaker.

7.2 Place the beaker and sample in a muffle furnace and set the temperature to 210°C.

7.3 Carbonize the sample by allowing it to remain at 210°C for 8 h.

7.4 Raise the temperature of the furnace to 375°C and allow the sample to ash at this temperature for 16 h. Finally, ash at 525°C for 24 h.

7.5 Transfer the ashed sample to a 250-mL Teflon beaker.

7.6 Add 25 mL of concentrated HNO_3 and 25 mL of concentrated HF.

Note: Paper filters might be completely soluble in HNO_3, in which case the addition of HF may be excluded, and the procedure can be continued at Section 7.14.

7.7 Place the sample on a hot plate and take to dryness.

7.8 Repeat the steps in Sections 7.6 and 7.7 twice.

7.9 Add 15 mL of concentrated HNO_3 and take to dryness.

7.10 Repeat Section 7.9 twice.

7.11 Take up the residue in 25 mL of 8 M HNO_3 and 3 to 5 mL of 30 percent H_2O_2.

7.12 Transfer the sample to the original ashing beaker.

7.13 Place the beaker on a hot plate and digest with the addition of 30 percent H_2O_2 in 1-mL portions until the solution is clear.

7.14 Add 1.00 mL of 10 dpm per mL ^{242}Pu tracer solution.

7.15 Adjust the volume to about 50 mL and the acidity to 8 M HNO_3 by evaporation and/or the addition of concentrated HNO_3.

7.16 Add 250 mg of $NaNO_2$ crystals, place on a hot plate, bring to a boil rapidly, immediately remove from heat, and allow the sample to digest for 20 min to adjust the valence of plutonium to Pu^{+4}.

7.17 While the sample is digesting, prepare a resin column as follows:

7.17.1 Place a glass-wool plug in the bottom of the column described in Section 5.9.3.

7.17.2 Slurry the resin (see Section 6.14) with water and immediately discard the fines by decanting. Repeat as necessary until fines are removed.

7.17.3 Transfer 4 mL of resin to the column with water. Prevent any channeling by maintaining the solution level above the resin by use of the stopcock.

7.17.4 Place a glass-wool plug on top of the resin.

7.17.5 Convert the resin to the nitrate form by passing several column volumes of 8 M HNO_3 through the column until the resin is free of chloride ions.

7.18 Transfer the sample solution, which should be at room temperature, to the prepared resin column, and allow it to flow through the column at a rate of 2 mL per min. Discard the effluent solution.

7.19 Rinse the beaker with 25 mL of 8 M HNO_3 and transfer the rinse to the column. Allow the 8 M HNO_3 rinse to flow through the column at a rate of 2 mL per min. Discard the effluent solution.

7.20 Rinse the beaker with 25 mL of 8 M HCl and transfer the rinse to the column. Allow the 8 M HCl rinse to flow through the column at a rate of 2 mL per min. Discard the effluent solution.

7.21 Add one drop of 0.1 M $Fe(NO_3)_3$ and 1 mL of 5 M $NH_2OH{\cdot}HCl$ to the column. Open the stopcock and allow the solution to drain to the top of the resin bed, then stop the flow. Discard the effluent solution.

7.22 Add 4 mL of 0.5 M HCl 0.05 M $NH_2OH \cdot HCl$ solution. Place a 50-mL glass centrifuge tube under the column. Allow 3 mL of solution to drain into the tube, and close the stopcock.

7.23 Allow a 20-min digestion time for reduction of the plutonium to Pu^{+3}.

7.24 Add 25 mL of 0.5 M HCl-0.05 M $NH_2OH \cdot HCl$ solution. Pass the solution through the column at a flow rate of 2 mL/min into the 50-mL tube.

7.25 Add 1 mL of praseodymium carrier to the sample solution in the 50-mL tube and mix thoroughly.

7.26 Add concentrated NH_4OH with stirring to a pH of 9.0. Allow a 15-min digestion time.

7.27 Centrifuge for 10 min at 1500 rpm and discard the supernatant solution.

7.28 Wash the precipitate with water, centrifuge, and discard the water wash solution.

7.29 Dissolve the precipitate in 6 drops of concentrated HNO_3 and transfer the dissolved sample to a 50-mL extraction vial with 5 mL of 1 M HNO_3. Add 10 drops of 3 M $NaNO_2$, mix well, and allow a 20-min digestion time for plutonium to oxidize to Pu^{+4}.

7.30 Add 1 mL of 0.5 M TTA-xylene solution and extract on a Vortex mixer for 10 min.

7.31 Centrifuge for 2 min to separate the phases. Discard the aqueous phase.

7.32 Scrub the TTA extract with 5 mL of 1 M HNO_3. Centrifuge and discard the aqueous phase.

7.33 Transfer the TTA to a stainless-steel disc placed on a hot plate set at 150°C. Allow the TTA to dry thoroughly.

7.34 Flame the stainless steel disc to a red heat.

7.35 Measure the alpha activities by pulse height analysis with a silicon surface-barrier detector coupled to a multichannel analyzer.

8.0 CALCULATIONS

8.1 Plutonium on the total filter sample.

$$
\begin{aligned}
{}^{238}\mathrm{Pu},\ \mathrm{pCi} &= A\cdot K\cdot C/D \\
{}^{239}\mathrm{Pu},\ \mathrm{pCi} &= B\cdot K\cdot C/D
\end{aligned}
$$

where:

A = Net integrated counts of ^{238}Pu from pulse analysis

B = Net integrated counts of ^{239}Pu from pulse analysis

C = dpm of ^{242}Pu added

D = Net integrated counts of ^{242}Pu from pulse analysis

K = Conversion factor to pCi = 1 pCi/2.22 dpm.

8.2 Plutonium in air:

$$
\begin{aligned}
{}^{238}\mathrm{Pu},\ \mathrm{pCi/m^3} &= A\cdot K\cdot C/D\cdot E \\
{}^{239}\mathrm{Pu},\ \mathrm{pCi/m^3} &= B\cdot K\cdot C/D\cdot E
\end{aligned}
$$

where:

E = volume of air (m^3).

0 PRECISION AND ACCURACY

9.1 The precision is estimated to be +20 percent.

9.2 The accuracy has not been established.

10.0 REFERENCES

1. Johns, Frederic B., (Ed), February 1975. Handbook of Radiochemical Analytical Methods, EPA-680/4-75-001.

2. Coleman, George H., September 1, 1965. "The Radiochemistry of Plutonium," National Academy of Sciences - National Research Council, NAS-NS 3058.

3. Harley, John H., (Ed), 1972 (or later). EML Procedures Manual, HASL-300.

DETERMINATION OF PLUTONIUM IN WATER

1.0 SCOPE AND APPLICATION

1.1 This method is used for determining fallout levels of plutonium in water samples. Water containing <1 to 10 fCi/L of ^{239}Pu has been analyzed.

2.0 SUMMARY OF METHOD

2.1 ^{242}Pu tracer is added to previously filtered and acidified water samples. The isotopes of plutonium are chemically separated from a sample by coprecipitation with calcium fluoride, anion exchange, and electrodeposition. The plated plutonium is analyzed by alpha-spectrometry.

3.0 APPARATUS AND EQUIPMENT

3.1 Hot plates.

3.2 Ion-exchange columns.

3.3 DC power supply - 0 to 12 V, 0 to 2 amp.

3.4 Electrodeposition cell assembly - Consisting of disposable plastic vial, cap assembly containing stainless-steel holder for plating planchet (cathode), and Teflon cover with platinum electrode (anode).

3.5 3/4-in. stainless steel prepolished planchets.

3.6 Centrifuge.

3.7 Analytical balance.

3.8 Alpha-spectrometer with multichannel analyzer and printer.

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4.0 REAGENTS

4.1 Plutonium-242 standard solution.

4.2 Concentrated HNO_3.

4.3 Concentrated HCl.

4.4 $Na_2S_2O_7$.

4.5 NaF.

4.6 $Ca(NO_3)_2 \cdot 4H_2O$.

4.7 Aluminum nitrate-nitric acid reagent prepared by saturating 8 N HNO_3 with reagent grade $Al(NO_3)_3 \cdot 9H_2O$. This solution is purified by pouring it through a nitrate form AG-1-X8 anion exchange resin column.

4.8 Anion exchange resin type AG-1-X8, 100-200 mesh, chloride form.

4.9 8 N HNO_3.

4.10 0.1 N HCl-0.01 N HF.

4.11 5 w/o $NaHSO_4$.

4.12 15 w/o Na_2SO_4.

4.13 25 w/o KOH

4.14 5 w/o NH_4OH.

4.15 Deionized water.

4.16 Ethyl alcohol.

4.17 Acetone.

5.0 PROCEDURE

5.1 Sample Preparation

5.1.1 A sample of suitable size, 5 L, is taken and filtered if solids are present. (All samples are acidified with 5 mL/L of concentrated HNO_3 at time of collection.)

5.1.2 The previously acidified sample is made 0.12 N in HNO_3 by the addition of 12.5 mL concentrated HNO_3 per 5 L volume of water. A known amount of ^{242}Pu tracer is also added.

5.1.3 The sample is placed on a stirrer-hot plate, a magnetic stirring bar is added, and the sample is stirred. Next, 5 g of $Na_2S_2O_7$ per liter of sample is added and the sample heated at 45 to 50°C for at least 4 h.

5.1.4 After 4 h, the heating is stopped, but stirring is continued with the addition of 4 g of NaF per liter of sample. This should dissolve in 10 min.

5.1.5 After NaF dissolution, 3 g of $Ca(NO_3)_2 \cdot 4H_2O$ is added and stirring continued for two more hours.

5.1.6 The CaF_2 precipitate is allowed to settle completely, preferably overnight.

5.1.7 Most of the supernate is removed by siphoning. The precipitate is washed from the large container into a smaller beaker with water and then centrifuged using 50 mL centrifuge tubes.

5.1.8 The CaF_2 precipitate is dissolved by heating with 30 mL of aluminum nitrate-nitric acid solution.

5.2 Ion Exchange Column Preparation

5.2.1 Sufficient AG-1X8, 100-200 mesh, chloride form, anion exchange resin is slurried with water to make a 1-cm I.D. column, 10-cm long.

5.2.2 The slurry is added to the column, the resin is allowed to settle for a few seconds, and the stopcock opened. The column is rinsed with water and drained to the top of the resin.

5.2.3 The resin is converted to the nitrate form by the addition of 60 mL of 8 N HNO_3 and drained to the top of the resin.

5.3 Ion Exchange Separation

5.3.1 The cooled solution from step 5.1.8 is added to the column and drained to the top of the column.

5.3.2 The column is washed with 100 mL of 8 N HNO_3 and drained to the top of the column.

5.3.3 The column is next washed with 100 mL of concentrated HCl and drained to the top of the column.

5.3.4 The plutonium is removed from the column with 30 mL of 0.1 N HCl-0.01 N HF, which is collected in a small beaker and evaporated to dryness on a hot plate.

5.3.5 The residue is redissolved in a small volume of concentrated HNO_3 and evaporated to dryness on a hot plate. This is repeated two more times.

5.4 Electrodeposition of Plutonium

5.4.1 A 3/4-in. stainless steel planchet is inscribed with sample I.D. and wiped clean with acetone.

5.4.2 The planchet is assembled in the cell as the cathode and the cell is rinsed with distilled water several times.

5.4.3 The assembled cell is wiped dry on the outside and water is introduced into it and allowed to stand for a short period of time. This will indicate if any leaks are present.

5.4.4 To the evaporated sample from Section 5.3.5, 2.5 mL of 5 w/o $NaHSO_4$, 4 mL of deionized water, and 5 mL of 15 w/o Na_2SO_4 are added. The solution is heated gently on the hot plate.

5.4.5 The electrolyte is transferred to the leak-pretested cell with 2 or 3 washings of 1 mL of deionized water, adding the rinses to the cell.

5.4.6 The platinum anode is inserted into the solution and the electrodes are connected to the source of current.

5.4.7 The power is turned on and the current is adjusted to 0.5 amp. Electrodeposition is continued for 5 min and then the current is increased to 0.75 amp.

5.4.8 Electrodeposition is continued for 60 to 90 min and then the current is reduced to 0.5 amp. Two mL of 25 w/o KOH is then added dropwise to stop the reaction. Deposition is continued for 1 min after the addition.

5.4.9 The power supply is shut off and the electrolyte is decanted into a waste container. The cell is washed three times with small amounts of 5 w/o NH_4OH.

5.4.10 The stainless steel planchet is removed and rinsed with an additional amount of 5 w/o NH_4OH and finally with ethyl alcohol.

5.4.11 The planchet is dried on a hot plate for 5 min at 200°C and cooled.

5.5 Alpha Counting

5.5.1 The sample is counted in the precalibrated alpha-spectrometer for up to 1000 min.

5.5.2 After the desired counting time, the data accumulated in the multi-channel analyzer are printed out.

6.0 CALCULATIONS

6.1 Using the printout data (Section 5.5.2), the counts per minute (cpm) of ^{242}Pu tracer and the cpm of ^{239}Pu and/or ^{238}Pu are determined.

6.2 The disintegrations per minute (dpm) of ^{242}Pu added as a tracer in Section 5.1.2 are calculated.

6.3 Using previously determined backgrounds for the ^{242}Pu, ^{239}Pu, and ^{238}Pu regions, the net counting rate for the respective regions is calculated.

The ^{239}Pu and/or ^{238}Pu concentrations in pico-Curies per liter (pCi/L) are calculated by using the following equation:

$$\text{Pu pCi/L} = \frac{A \times C}{B \times V \times 2.22}$$

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where:

A = Net counts per min of ^{239}Pu or ^{238}Pu

B = Net counts per min ^{242}Pu

C = DPM of ^{242}Pu tracer

V = Volume of sample taken (L).

7.0 REPORTING

7.1 Results are reported on the standard ACL Report of Analytical Results, Form No. CMT-84 (10-84).

8.0 QUALITY ASSURANCE/QUALITY CONTORL

8.1 Reagent blanks are run whenever a new batch of reagent is used.

8.2 EPA performance evaluation samples are analyzed on a regular basis.

8.3 Alpha-spectrometer backgrounds are taken regularly, most often over the weekend for 3000 min.

9.0 PRECISION AND ACCURACY

9.1 Precision in analyzing water samples is limited only by the statistics of the number of alpha-counts obtained in the ^{239}Pu and ^{238}Pu peaks in the spectra obtained by the alpha-spectrometer. Therefore, the size analyzed has a direct bearing on the precision.

10.0 REFERENCES

1. Golchert, N.W. and J. Sedlet, 1972. "Radiochemical Determination of Plutonium in Environmental Water Samples," Radiochem. Radioanal. Letters, 12, 215.

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2. Kressin, Ivan K., May 1977. "Electrodeposition of Plutonium and Americium for High Resolution Alpha-Spectrometry," *Anal. Chem*. *49*, No. 6.

3. Golchert, N. W., T. L. Duffy, and J. Sedlet, "1985 Annual Site Environmental Report for Argonne National Laboratory," ANL-86-13.

DETERMINATION OF PLUTONIUM IN SEDIMENT AND SOIL

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the determination of plutonium in soils and sediments.

1.2 At Oak Ridge National Laboratory (ORNL), the lowest concentration reported is 0.004 pCi/g when analyzing a 10-g sample, using 10 dpm of plutonium-242 tracer, counting for 1000 min on an alpha pulse-height analyzer with a detector having a 20 percent efficiency and a 0.005-cpm background over each energy region of interest, and realizing an 80 percent chemical recovery of the plutonium.

1.3 At other plants, the lowest concentration reported is 0.02 pCi/g for 10-g samples.

2.0 SUMMARY OF METHOD

2.1 A known quantity of plutonium-242 tracer, which is used as an internal standard, is added to the sample that is leached by hot nitric acid and hot nitric acid-hydrogen peroxide treatment. After being leached, plutonium is adjusted to Pu^{+4}, adsorbed on anion exchange resin, reduced to Pu^{+3}, and selectively eluted from the resin. Subsequently, plutonium is carried on praseodymium hydroxide, dissolved, and oxidized to Pu^{+4} which is then extracted with thenoyltrifluoroacetone-xylene. The organic extract is deposited on a stainless-steel disc and the plutonium is determined by alpha spectrometry.

3.0 INTERFERENCES

3.1 Samples which are of a refractory nature, such as test-site materials, are not apt to release plutonium in the leaching process; therefore, more rigorous treatment is recommended for decomposition of these samples.

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3.2 Plutonium-240 cannot be distinguished from plutonium-239 by alpha pulse-height analysis; however, alpha pulse-height analysis eliminates most other alpha interferences.

4.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

4.1 The samples are oven-dried to a constant weight at 105°C, pulverized, and screened to 100-mesh particle size.

4.2 The dried and screened sample material is stored in airtight glass or plastic containers.

5.0 APPARATUS AND EQUIPMENT

5.1 Drying oven - Capable of maintaining a temperature of 105°C.

5.2 Muffle furnace - Capable of maintaining a temperature of 500°C.

5.3 Hot plate with magnetic stirrer.

5.4 Centrifuge.

5.5 Vortex mixer.

5.6 Extraction vials - 50-mL with plastic-lined screw caps.

5.7 Screens - 40- and 100-mesh.

5.8 Transfer pipets.

5.9 Laboratory glassware

5.9.1 Beakers - 250-mL size and 500-mL tall-form.

5.9.2 Centrifuge tubes - 50-mL glass and 100-mL plastic.

5.9.3 Glass ion-exchange column - 8-mm I.D. by 25-cm long, fitted with a stopcock and reservoir.

5.10 Stainless steel counting discs.

5.11 Multichannel analyzer system with silicon surface-barrier detector(s).

5.12 Analytical balance.

5.13 Magnetic stirring bar, Teflon coated, 1-1/2-in. long.

6.0 REAGENTS

6.1 Nitric acid - Concentrated.

Nitric acid, 8 M - Add 500 mL of concentrated HNO_3 to 450 mL of water and dilute to 1 L.

6.3 Ammonium hydroxide - Concentrated.

6.4 Plutonium-242 tracer solution - Use NBS SRM 4334, 4335, or their replacement; or use an equivalent solution of ^{242}Pu. Prepare a standard in the range of 10 to 25 dpm per milliliter in 2 M HNO_3 and store in glass.

6.5 Nitric acid (1 M) - Add 62.5 mL of concentrated HNO_3 to 500 mL of water and dilute to 1 L.

6.6 Sodium nitrite - $NaNO_2$ crystals.

6.7 Sodium nitrite solution (3 M) - Dissolve 10.4 g of sodium nitrite ($NaNO_2$) in water and dilute to 50 mL. Prepare a fresh solution daily.

6.8 Thenoyltrifluoroacetone (TTA)-xylene solution (0.5 M TTA) - Dissolve 111 grams of $Sc_4H_3COCH_2COCF_3$ (TTA) in xylene and dilute to 1 L with xylene.

6.9 Ferric nitrate solution, 0.1 M - Dissolve 40.4 g of ferric nitrate nonahydrate $[Fe(NO_3)_3 \cdot 9H_2O]$ in water and dilute to 1 L.

6.10 Hydroxylamine-hydrochloride solution (5 M) - Dissolve 347.5 g of hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) in water and dilute to 1 L.

6.11 Hydrochloric acid-hydroxylamine hydrochloride solution, 0.5 M 0.5 M HCl - HCl-0.05 M NH_2OH-HCl - Add 42 mL of concentrated HCl and 10mL of 5 M NH_2OH-HCl to 1 L.

6.12 Hydrochloric acid - Concentrated.

6.13 Praseodymium carrier solution - Dissolve 12.82 g of praseodymium nitrate dihydrate $[Pr(NO_3)_3 \cdot 2H_2O]$ in 500 mL of water and dilute to 1 L.

6.14 Anion exchange resin - Dowex 1-X4 (50-100 mesh, chloride form) or equivalent.

6.15 Hydrochloric acid (8 M) - Add 666 mL of concentrated HCl to 300 mL of water and dilute to 1 L.

6.16 Hydrogen peroxide - 30 percent solution.

7.0 PROCEDURE

7.1 Transfer to exact weight (5- to 10-g range) of the 100-mesh sample to a 500-mL tall-form beaker. If the sample shows signs of containing organic matter, ash in a muffle furnace at 500°C for several hours before continuing.

7.2 Slowly add 50 to 75 mL of 8 M HNO_3 and allow sufficient time for any foaming to subside.

7.3 Add 1 mL of the ^{242}Pu standard tracer solution.

7.4 Carefully introduce the magnetic stirring bar, place on the hot plate, and digest with stirring at 90 to 95°C for 1 h.

7.5 Remove from the hot plate and transfer the solution to a 100-mL plastic centrifuge tube.

7.6 Centrifuge for 10 min at 1500 rpm.

7.7 Decant the supernatant liquid into a 250-mL beaker and retain it.

7.8 Rinse the residue from the centrifuge tube into the original 500-mL beaker with 50 to 75 mL of 8 M HNO_3.

7.9 Return to the hot plate and digest while stirring at 90 to 95°C for 1 h and adding a few drops of 30 percent hydrogen peroxide intermittently for a total of 5 to 10 mL.

7.10 Repeat the steps in Sections 7.5 through 7.7.

7.11 Repeat the step in Section 7.8 using 25 mL of 1 M HNO_3.

7.12 Repeat the steps in Sections 7.9 and 7.10 and discard the residue.

7.13 Add 250 mg of $NaNO_2$ crystals, place on a hot plate, rapidly bring to a boil, immediately remove from heat, and allow the sample to digest for 20 min to adjust the valence of plutonium to Pu^{+4}.

7.14 While the sample is digesting, prepare a resin column as follows:

7.14.1 Place a glass-wool plug in the bottom of the column described in Section 5.9.3.

7.14.2 Slurry the resin (Section 6.14) with water and immediately discard the fines by decanting. Repeat as necessary until fines are removed.

7.14.3 Transfer 4 mL of resin to the column with water. Prevent any channeling by maintaining the solution level above the resin by use of the stopcock.

7.14.4 Place a glass-wool plug on top of the resin.

7.14.5 Convert the resin to the nitrate form by passing several column volumes of 8 M HNO_3 through the column until the resin is free of chloride ions.

7.15 Transfer the sample solution, which should now be at room temperature, to the prepared resin column and allow it to flow through the column at a rate of 2 mL per minute. Discard the effluent solution.

7.16 Rinse the beaker with 25 mL of 8 M HNO_3 and transfer the rinse to the column. Allow the 8 M HNO_3 rinse to flow through the column at a rate of 2 mL per minute. Discard the effluent solution.

7.17 Rinse the beaker with 25 mL of 8 M HCL and transfer the rinse to the column. Allow the 8 M HCl rinse to flow through the column at a rate of 2 mL per minute. Discard the solution.

7.18 Add one drop of 0.1 M $Fe(NO_3)_3$ and 1 mL of 5 M $NH_2OH.HCl$ solution. Open the stopcock and allow the solution to drain to the top of the resin bed; then stop the flow. Discard the effluent solution.

7.19 Add 4 mL of 0.5 M HCl-0.05 M $NH_2OH \cdot HCl$ solution. Place a 50-mL glass centrifuge tube under the column. Allow 3 mL of solution to drain into the tube and close the stopcock.

7.20 Allow 20 min digestion time for reduction of the plutonium to Pu^{+3}.

7.21 Add 25 mL of 0.5 M HCl-0.05 M $NH_2OH \cdot HCl$ solution. Pass the solution through the column at a flow rate of 2 mL per minute into the 50-mL tube.

7.22 Add 1 mL of praseodymium carrier to the sample solution in the 50-mL tube and mix thoroughly.

7.23 Add concentrated NH_4OH while stirring to a pH of 9.0. Allow 15 min digestion time.

7.24 Centrifuge for 10 min at 1500 rpm and discard the supernatant solution.

7.25 Wash the precipitate with water, centrifuge, and discard the water wash solution.

7.26 Dissolve the precipitate in 6 drops of concentrated HNO_3 and transfer the dissolved sample to a 50-mL extraction vial with 5 mL of 1 M HNO_3. Add 10 drops of 3 M $NaNO_2$, mix well, and allow 20 min digestion time for plutonium to oxidize to Pu^{+4}.

7.27 Add 1 mL of 0.5 M TTA-xylene solution and extract on a Vortex mixer for 10 min.

7.28 Centrifuge for 2 min to separate the phases. Discard the aqueous phase.

7.29 Scrub the TTA extract with 5 mL of 1 M HNO_3. Centrifuge and discard the aqueous phase.

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7.30 Transfer all of the TTA to a stainless-steel disc placed on a hot plate set at 150°C. Allow the TTA to dry thoroughly.

7.31 Flame the stainless-steel disc to a red heat.

7.32 Measure the alpha activities by pulse height analysis with a silicon surface-barrier detector coupled to a multichannel analyzer.

8.0 CALCULATIONS

$$^{238}\text{Pu (pCi/g)} = A \cdot K \cdot C / D \cdot E$$
$$^{239}\text{Pu (pCi/g)} = B \cdot K \cdot C / D \cdot E$$

where:

A = Net integrated counts of ^{238}Pu from pulse analysis

B = Net integrated counts of ^{239}Pu from pulse analysis

C = DPM of ^{242}Pu added

D = Net integrated counts of ^{242}Pu from pulse analysis

E = Weight of sample (g)

K = Conversion factor to pCi = 1 pCi/2.22 dpm.

9.0 PRECISION AND ACCURACY

9.1 The precision is estimated to be ±20 percent.

9.2 The accuracy has not been established.

10.0 REFERENCES

1. Johns, Frederic B., (Ed), February, 1975. Handbook of Radiochemical Analytical Methods, EPA-680/4-75-001.

2. Coleman, George H., September 1, 1965. The Radiochemistry of Plutonium, National Academy of Sciences, National Research Council, NAS-NS 3058.

3. Harley, John H., (Ed), 1972. HASL Procedures Manual, HASL-300.

DETERMINATION OF URANIUM ISOTOPES IN WATER

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the determination of uranium isotopes in potable, natural, and industrial waters.

1.2 At Oak Ridge National Laboratories (ORNL), the lowest concentration reported of uranium isotopes in water is 4 x 10^{-5} pCi/mL when analyzing a 1-L sample, using 10 dpm of uranium-232 tracer, counting for 1000 min on an alpha pulse-height analyzer with a detector having a 20 percent efficiency and a 0.005-cpm background over each energy region of interest, and realizing an 80 percent chemical recovery of the uranium.

1.3 At other plants, the lowest reported concentration is 1 x 10^{-3} pCi/mL for a 1-L sample.

2.0 SUMMARY OF METHOD

2.1 The sample is equilibrated with ^{232}U which is used as an internal standard; subsequently uranium is chemically purified by use of anion exchange resin and repeated methyl isobutyl ketone (hexone) extractions. The extracted uranium is deposited on a stainless steel disc which is counted on a multichannel analyzer using a silicon surface-barrier detector to determine the uranium concentration.

3.0 INTERFERENCES

3.1 Iron in mg/mL concentrations tends to follow uranium through the chemical separations, causing serious degradation of alpha measurements.

3.2 Alpha pulse-height analysis eliminates interferences from other alpha emitters.

4.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

4.1 If suspended and/or soluble uranium determinations are desired separately, the samples shall first be filtered to remove the suspended particulates as soon as practicable; then the samples shall be immediately adjusted to a pH of 1.0 with nitric acid.

4.2 If total uranium determinations are desired, the samples shall be adjusted to a pH of 1.0 as soon as practicable without filtering.

4.3 After pH adjustments, the samples are stored in glass or plastic containers.

5.0 APPARATUS AND EQUIPMENT

5.1 Glass ion-exchange column - 8-mm I.D. by 25-cm long, fitted with a stopcock and reservoir.

5.2 Centrifuge.

5.3 Vortex mixer.

5.4 Hot plate.

5.5 Stainless steel counting discs.

5.6 Extraction vials - 50 mL with plastic-lined screw caps.

5.7 Transfer pipets.

5.8 Beakers - 100 mL, 250 mL and a size to accommodate sample aliquot.

5.9 Multichannel analyzer system with silicon surface-barrier detector(s).

[illegible].0 REAGENTS

6.1 Nitric acid - concentrated.

6.2 Nitric acid (8 M) - Add 500 mL of concetrated HNO_3 to 500 mL of water.

6.3 Aluminum nitrate solution (2.8 M) - Dissolve 1050 g of aluminum nitrate nanohydrate [$Al(NO_3)_3 \cdot 9H_2O$] in a minimum of water with heat. Cautiously add 100 mL of concentrated NH_4OH with stirring. Continue heating and stirring until all of the precipitate dissolves, and then dilute to 1 L with water.

6.4 Sodium nitrite - $NaNO_2$ crystals.

6.5 Methyl isobutyl ketone (hexone).

6.6 Potassium bromate - $KBrO_3$ crystals.

6.7 Uranium-232 tracer solution - Dilute a stock solution of ^{232}U to a concentration of 10-dpm/mL.

6.8 Anion exchange resin - Dowex 1-X4 (50 to 100 mesh, chloride form) or equivalent.

7.0 PROCEDURE

7.1 Transfer a measured aliquot of the sample to an adequately sized beaker and adjust the acidity to 0.1 molar with concentrated HNO_3.

7.2 Add 1 mL of 10/mL ^{232}U tracer solution.

7.3 Place on a hot plate which is covered with an asbestos mat and take to dryness. (An alternate method for volume reduction is to coprecipitate uranium on iron hydroxide. Caution: Iron interferes--see Section 3.0.)

7.4 Dissolve the residue in 25 mL of 8 M HNO_3.

7.5 Add 0.5 g of $NaNO_2$ crystals and heat to boiling.

7.6 Remove from heat and allow 20 min digestion time.

7.7 While the sample is digesting, prepare a resin column as follows:

   7.7.1 Place a glass-wool plug in the bottom of the column described in Section 5.1.

   7.7.2 Slurry the resin (see Section 6.8) with water and immediately discard the fines by decanting. Repeat as necessary until fines are removed.

   7.7.3 Transfer 4 mL of the resin to the column with water. Prevent any channeling by maintaining the solution level above the resin with the stopcock.

   7.7.4 Place a glass-wool plug on top of the resin.

   7.7.5 Convert the resin to the nitrate form by passing several column volumes of 8 M HNO_3 through the column until the resin is free of chloride ions.

7.8 Transfer the sample solution, which shall be cooled at room temperature, to the prepared resin column.

7.9 Place a 250-mL beaker beneath the column and allow the sample solution to drain into the beaker at a flow rate of 2 mL/min.

7.10 Rinse the beaker with 25 mL of 8 M HNO_3 and transfer the rinse to the column.

7.11 Allow the rinse to drain into the beaker also.

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7.12 Place the beaker containing the column effluent on a hot plate and take to dryness.

7.13 Dissolve the residue in 10 mL of $Al(NO_3)_3$ solution and transfer to an extraction vial using a minimum of $Al(NO_3)_3$ to rinse the beaker.

7.14 Add an equal volume of hexone and extract on a Vortex mixer for 10 min.

7.15 Centrifuge for 2 min to separate the phases and discard the aqueous phase.

7.16 Add an equal volume of water and back-extract into the water on a Vortex mixer for 10 min.

7.17 Centrifuge for 2 min to separate the phases.

7.18 Transfer the aqueous phase to a 100-mL beaker.

7.19 Repeat Sections 7.16, 7.17, and 7.18.

7.20 Place the beaker containing the water strip solution on a hot plate and take to dryness.

7.21 Add enough 8 M HNO_3 to moisten the residue.

7.22 Add 10 to 20 mg of $KBrO_3$ crystals and digest for 10 min.

7.23 Dissolve and transfer the residue to an extraction vial with 5 mL $Al(NO_3)_3$ of solution.

7.24 Repeat Section 7.14 using 1 mL of hexone; repeat Section 7.15.

7.25 Transfer the entire hexone extract dropwise to a stainless steel disc placed on a hot plate set at 100°C.

7.26 Flame the disc to a red heat.

7.27 Measure the uranium alpha activities by pulsing with a silicon surface-barrier detector and multichannel analyzer.

8.0 CALCULATIONS

8.1 Uranium isotopes in potable, natural, and industrial waters will be calculated using the following equation.

$$^{238}\mathrm{U},\ \mathrm{pCi/mL} = A \cdot K \cdot E / D \cdot V$$

$$^{235}\mathrm{U},\ \mathrm{pCi/mL} = B \cdot K \cdot E / D \cdot V$$

$$^{234}\mathrm{U},\ \mathrm{pCi/mL} = C \cdot K \cdot E / D \cdot V$$

where:

A = Net integrated counts of ^{238}U from pulse analysis

B = Net integrated counts of ^{235}U from pulse analysis

C = Net integrated counts of ^{234}U from pulse analysis

D = Net integrated counts of ^{232}U from pulse analysis

E = ^{232}U tracer added (dpm)

K = Conversion factor to pCi = 1 pCi/2.22 dpm

V = Volume of sample (mL).

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9.0 PRECISION AND ACCURACY

9.1 The precision of this method is estimated to be ± 15 percent.

9.2 The accuracy of this method has not been established; however, repeated determinations on materials of known concentration do not indicate a significant bias.

10.0 REFERENCES

1. Gindler, J. E., March, 1962. The Radiochemistry of Uranium, NAS-NS 3050.

2. Johns, F. B., Editor, February, 1975. Handbook of Radiochemical Methods, EPA-680/4-75-001.

DETERMINATION OF URANIUM ISOTOPES IN SEDIMENT AND SOIL
(Method EC-378)

1.0 SCOPE AND APPLICATION

1.1 This method is applicable for determining the presence of uranium isotopes in soil and sediment samples.

1.2 At Oak Ridge National Laboratory (ORNL), the lowest reported concentration of uranium isotopes in soil and sediment samples is 0.004 pCi/mL when analyzing a 10-g sample, using 10 dpm of uranium-232 tracer, counting for 1000 min on an alpha pulse-height analyzer with a detector having a 20 percent efficiency and a 0.005-cpm background over each energy region of interest, and realizing an 80 percent chemical recovery of the uranium.

1.3 At other UCC-ND plants, the lowest reported concentration of uranium isotopes in soil and sediment samples is 0.02 pCi/g for 10-g samples.

2.0 SUMMARY OF METHOD

2.1 A known quantity of uranium-232 tracer, used as an internal standard, is added to the sample which is leached by hot nitric acid and hot nitric acid-hydrogen peroxide treatment. The leaching solution is passed through an anion exchange resin to absorb plutonium and thorium, leaving purified uranium in the effluent solution. The uranium is further purified by repeated extractions with methyl isobutyl ketone (hexone). The final hexone extract is dried on a stainless steel disc which is counted on a multichannel analyzer system using a silicon surface-barrier detector to determine the uranium concentration.

3.0 INTERFERENCES

3.1 Indigenous uranium is not likely to be reached by the leaching process; therefore, more rigorous dissolution methods shall be used for its determination.

3.2 Iron in mg/g concentrations tends to follow uranium throughout the chemical separations and causes serious degradation of alpha measurements.

3.3 Uranium-234 cannot be distinguished easily from uranium-233 by alpha pulse-height analysis.

4.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

4.1 The samples are oven-dried to a constant weight at 105°C, pulverized, screened to 100-mesh particle size, and thoroughly blended.

4.2 The prepared sample materials are stored in airtight glass or plastic containers.

5.0 APPARATUS AND EQUIPMENT

5.1 Drying oven - 105°C.

5.2 Muffle furnace - 500°C.

5.3 Hot plate with magnetic stirrer.

5.4 Centrifuge.

5.5 Vortex mixer.

5.6 Extraction vials - 50 mL with plastic-lined screw caps.

5.7 Screens - 40 and 100 mesh.

5.8 Transfer pipets.

5.9 Laboratory Glassware

  5.9.1 Beakers - 250-mL size and 500-mL tall-form.

  5.9.2 Centrifuge tubes - 50 mL glass and 100 mL plastic.

  5.9.3 Glass ion-exchange column - 8-mm I.D. by 25-cm long, fitted with a stopcock and reservoir.

5.10 Stainless steel counting discs.

5.11 Multichannel analyzer system with silicon surface-barrier detector(s).

5.12 Analytical balance.

5.13 Magnetic stirring bar - Teflon-coated, 1-1/2-in. long.

6.0 REAGENTS

6.1 Nitric acid - Concentrated.

6.2 Nitric acid (8 M) - Add 500 mL of concentrated HNO_3 to 500 mL of water.

6.3 Aluminum nitrate solution (2.8 M) - Dissolve 1050 grams of aluminum nitrate nanohydrate [$Al(NO_3)_3 \cdot 9H_2O$] in a minimum of water with heat. Cautiously add 100 mL of concentrated NH_4OH with stirring. Continue heating and stirring until all of the precipitate dissolves, and then dilute to 1 L with water.

6.4 Sodium nitrite - $NaNO_2$ crystals.

6.5 Methyl isobutyl ketone (hexone).

6.6 Potassium bromate - $KBrO_3$ crystals.

6.7 Uranium-232 tracer solution - Dilute a stock solution of ^{232}U to a concentration of 10 dpm/mL.

6.8 Anion exchange resin - Dowex 1-X4 (50 to 100 mesh, chloride form) or equivalent.

6.9 Hydrogen peroxide - 30 percent solution.

7.0 PROCEDURE

7.1 Transfer a measured weight (5 to 10 g) of the 100-mesh sample to a 500-mL tall-form beaker. If the sample is thought to contain organic matter, ash in a muffle furnace at 500°C for several hours before continuing.

7.2 Slowly add 50 to 75 mL of 8 M HNO_3 allowing sufficient time for any foaming to subside.

7.3 Add 1 mL of 10-dpm/mL ^{232}U tracer solution.

7.4 Carefully introduce the magnetic stirring bar, place on the hot plate, and digest with stirring at 90° to 95°C for 1 h.

7.5 Remove from the hot plate and transfer the sample solution to a 100-mL plastic centrifuge tube.

7.6 Centrifuge for 10 min at 1500 rpm.

7.7 Decant the supernatant liquid into a 250-mL beaker and retain.

7.8 Rinse the residue from the centrifuge tube into the original 500-mL beaker with 50 to 75 mL of 8 M HNO_3.

7.9 Return to the hot plate and digest with stirring at 90° to 95°C for 1 h with the addition of a few drops of 30 percent hydrogen peroxide intermittently for a total of 5 to 10 mL.

7.10 Repeat Sections 7.5 through 7.7.

7.11 Repeat Sections 7.8 using 25 mL of 1 M HNO_3.

7.12 Repeat Sections 7.9 and 7.10 and discard the residue.

7.13 Add 250 mg of $NaNO_2$ crystals, place on hot plate, bring to a boil rapidly, immediately remove from heat, and allow the sample to digest for 20 min.

7.14 While the sample is digesting, prepare a resin column as follows:

7.14.1 Place a glass-wool plug in the bottom of the column described in Section 5.9.3.

7.14.2 Slurry the resin (see Section 6.8) with water and immediately discard the fines by decanting. Repeat as necessary until fines are removed.

7.14.3 Transfer 4 mL of the resin to the column with water. Prevent any channeling by maintaining the solution level above the resin by using the stopcock.

7.14.4 Place a glass-wool plug on top of the resin.

7.14.5 Convert the resin to the nitrate form by passing several column volumes of 8 M HNO_3 through the column until the resin is free of chloride ions.

7.15 Transfer the sample solution, cooled to room temperature, to the prepared resin column.

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7.16 Place a 250-mL beaker beneath the column and allow the sample solution to drain into the beaker at a flow rate of 2 mL/min.

7.17 Rinse the beaker with 25 mL of 8 M HNO_3 and transfer the rinse to the column.

7.18 Allow the rinse to drain into the beaker also.

7.19 Place the beaker containing the column effluent on a hot plate and take to dryness.

7.20 Dissolve the residue in 10 mL of $Al(NO_3)_3$ solution and transfer to an extraction vial, using a minimum of $Al(NO_3)_3$ to rinse the beaker.

7.21 Add an equal volume of hexone and extract on a Vortex mixer for 10 min.

7.22 Centrifuge for 2 min to separate the phases and discard the aqueous phase.

7.23 Add an equal volume of water and back-extract into the water on a Vortex mixer for 10 min.

7.24 Centrifuge for 2 min to separate the phases.

7.25 Transfer the aqueous phase to a 100-mL beaker.

7.26 Repeat Sections 7.23, 7.24, and 7.25.

7.27 Place the beaker containing the water strip solution on a hot plate and take to dryness.

7.28 Add enough 8 M HNO_3 to moisten the residue.

7.29 Add 10 to 20 mg of $KBrO_3$ crystals and digest for 10 min.

7.30 Dissolve and transfer the residue to an extraction vial with 5 mL of $Al(NO_3)_3$ solution.

7.31 Repeat Section 7.21 using 1 mL of hexone; repeat Section 7.22.

7.32 Transfer the entire hexone extract dropwise to a stainless steel disc placed on a hot plate set at 100°C.

7.33 Flame the disc to a red heat.

7.34 Measure the uranium alpha activities by pulsing with a silicon surface-barrier detector and multichannel analyzer.

8.0 CALCULATIONS

8.1 Uranium isotopes in soil sediments will be determined using the following equation.

$$^{238}U,\ pCi/g = A \cdot K \cdot E/D \cdot V$$

$$^{235}U,\ pCi/g = B \cdot K \cdot E/D \cdot V$$

$$^{234}U,\ pCi/g = C \cdot K \cdot E/D \cdot V$$

where:

A = Net integrated counts of ^{238}U from pulse analysis

B = Net integrated counts of ^{235}U from pulse analysis

C = Net integrated counts of ^{234}U from pulse analysis

D = Net integrated counts of ^{232}U from pulse analysis

E = ^{232}U tracer added (dpm)

K = Conversion factor to pCi = 1 pCi/2.22 dpm

V = Weight of sample (g).

9.0 PRECISION AND ACCURACY

9.1 The precision of this method is estimated to be ±15 percent.

9.2 The accuracy of this method has not been established; however, repeated determinations on materials of known concentration do not indicate a significant bias.

10.0 REFERENCES

1. Gindler, J. E., March, 1962. "The Radiochemistry of Uranium," NAS-NS 3050.

2. Johns, F. B., Editor, February, 1975. Handbook of Radiochemical Methods, EPA-680/4-75-001.

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DETERMINATION OF URANIUM ISOTOPES IN AIR FILTERS
(Method EC-287)

1.0 SCOPE AND APPLICATION

1.1 This method is applicable for determining the presence of the uranium isotopes of filter paper and Hollingsworth-type air filters.

1.2 At Oak Ridge National Laboratory (ORNL), the lowest reported concentration of uranium isotopes in air filters is 0.04 pCi/total filter sample, using 10 dpm of uranium-232 tracer, counting for 1000 min on an alpha pulse-height analyzer with a detector having a 20 percent efficiency and a 0.005-cpm background over each energy region of interest, and realizing an 80 percent chemical recovery of the uranium. Typically, for filters that have filtered 1×10^3 cubic meters of air, the lowest concentration reported is 4×10^{-5} pCi/m.

1.3 At other plants, the lowest reported concentration of uranium isotopes in air filters is 0.1 pCi/filter sample.

2.0 SUMMARY OF METHOD

2.1 Uranium-232 tracer is added to the dissolved sample solution and equilibrated with the uranium from the sample. Plutonium and thorium are separated by adsorption on anion-exchange resin under conditions that allow uranium to remain in the effluent. Repeated liquid-liquid extractions with methyl isobutyl ketone (hexone) are used to purify the uranium. The final hexone extract is dried on a stainless steel plate, and a determination of the uranium isotopes is made by alpha spectrometric measurements, using a silicon surface-barrier detector to count the plate.

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.0 INTERFERENCES

3.1 Iron in mg/g concentrations tends to follow uranium through the chemical separations and causes serious degradation of alpha measurements.

3.2 Uranium-234 cannot be distinguished easily from uranium-233 by alpha pulse-height analysis.

4.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

4.1 Filters shall be handled as little as possible to avoid loss of particulates and shall be stored in plastic containers such as polyethylene bags.

5.0 APPARATUS AND EQUIPMENT

5.1 Analytical balance.

5.2 Muffle furnace - capable of maintaining a temperature of 525°C.

5.3 Hot plate.

5.4 Centrifuge.

5.5 Vortex mixer.

5.6 Extraction vials - 50 mL with plastic-lined screw caps.

5.7 Teflon beakers - 250 mL.

5.8 Transfer pipets.

5.9 Laboratory glassware

5.9.1 Beakers - 100, 250, and 600 mL.

5.9.2 Centrifuge tubes - 50-mL glass.

5.9.3 Glass ion-exchange column - 8-mm I.D. by 25-cm long, fitted with a stopcock and reservoir.

5.10 Stainless steel counting discs.

5.11 Multichannel analyzer system with silicon surface-barrier detector(s).

6.0 REAGENTS

6.1 Nitric acid - Concentrated.

6.2 Nitric acid (8 M) - Add 500 ml of concentrated HNO_3 to 500 mL of water.

6.3 Aluminum nitrate solution (2.8 M) - Dissolve 1050 g of aluminum nitrate nanohydrate [$Al(NO_3)_3 \cdot 9H_2O$] in a minimum of water with heat. Cautiously add 100 mL of concentrated NH_4OH with stirring. Continue heating and stirring until all of the precipitate dissolves, and then dilute to 1 L with water.

6.4 Sodium nitrite - $NaNO_2$ crystals.

6.5 Methyl isobutyl ketone (hexone).

6.6 Potassium bromate - $KBrO_3$ crystals.

6.7 Uranium-232 tracer solution - Dilute a stock solution of ^{232}U to a concentration of 10 dpm/mL.

6.8 Anion exchange resin - Dowex 1-X4 (50 to 100 mesh, chloride form) or equivalent.

6.9 Hydrogen peroxide - 30 percent H_2O_2 solution.

6.10 Hydrofluoric acid - Concentrated.

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7.0 PROCEDURE

7.1 Place the filter material in an adequately sized beaker.

7.2 Place the beaker and sample in a muffle furnace and set the temperature at 210°C.

7.3 Carbonize the sample by allowing it to remain at 210°C for 8 h.

7.4 Raise the temperature of the furnace to 375°C and allow the sample to ash at this temperature for 16 h, and finally ash at 525°C for 24 h.

7.5 Transfer the ashed sample to a 250-mL Teflon beaker.

7.6 Add 25 mL of concentrated HNO_3 and 25 mL of concentrated HF.

Note: Paper filters might be completely soluble in HNO_3. If so, the addition of HF may be excluded, and the procedure can be continued at Section 7.14.

7.7 Place the sample on a hot plate and take to dryness.

7.8 Repeat Sections 7.6 and 7.7 twice.

7.9 Add 15 mL of concentrated HNO_3 and take to dryness.

7.10 Repeat Section 7.9 twice.

7.11 Take up the residue in 25 mL of 8 M HNO_3 and 3 to 5 mL of H_2O_2 solution.

7.12 Transfer the sample to the original ashing beaker.

7.13 Place the beaker on a hot plate and digest with the addition of 30 percent H_2O_2 in 1-mL portions until the solution is clear.

7.14 Add 1.00 mL of 10 dpm/mL ^{232}U tracer solution.

7.15 Adjust the acidity to 8 M HNO_3 by volume reducing the volume and/or adding concentrated HNO_3.

7.16 Add 250 mg of $NaNO_2$ crystals, place on hot plate, bring to a boil rapidly, immediately remove from heat, and allow the sample to digest for 20 min.

7.17 While the sample is digesting, prepare a resin column as follows:

  7.17.1 Place a glass-wool plug in the bottom of the column described in Section 5.9.3.

  7.17.2 Slurry the resin (see Section 6.8) with water and immediately discard the fines by decanting. Repeat as necessary until fines are removed.

  7.17.3 Transfer 4 mL of the resin to the column with water. Prevent any channeling by maintaining the solution level above the resin using the stopcock.

  7.17.4 Place a glass-wool plug on top of the resin.

  7.17.5 Convert the resin to the nitrate form by passing several column volumes of 8 M HNO_3 through the column until the resin is free of chloride ions.

7.18 Transfer the sample solution, cooled at room temperature, to the prepared resin column.

7.19 Place a 250-mL beaker beneath the column and allow the sample solution to drain into the beaker at a flow rate of 2 mL/min.

7.20 Rinse the beaker with 25 mL of 8 M HNO_3 and transfer the rinse to the column.

7.21 Allow the rinse to drain into the beaker also.

7.22 Place the beaker containing the column effluent on a hot plate and take to dryness.

7.23 Dissolve the residue in 10 mL of $Al(NO_3)_3$ solution and transfer to an extraction vial, using a minimum of $Al(NO_3)_3$ to rinse the beaker.

7.24 Add an equal volume of hexone, and extract on a Vortex mixer for 10 min.

7.25 Centrifuge for 2 min to separate the phases and discard the aqueous phase.

7.26 Add an equal volume of water and back-extract into the water on a Vortex mixer for 10 min.

7.27 Centrifuge for 2 min to separate the phases.

7.28 Transfer the aqueous phase to a 100-mL beaker.

7.29 Repeat Sections 7.26, 7.27, and 7.28.

7.30 Place the beaker containing the water strip solution on a hot plate and take to dryness.

7.31 Add enough 8 M HNO_3 to moisten the residue.

7.32 Add 10 to 20 mg of $KBrO_3$ crystals and digest for 10 min.

7.33 Dissolve and transfer the residue to an extraction vial with 5 mL of $Al(NO_3)_3$ solution.

7.34 Repeat Section 7.24 using 1 mL of hexone; repeat Section 7.25.

7.35 Transfer the entire hexone extract dropwise to a stainless steel disc placed on a hot plate set at 100°C.

7.36 Flame the disc to a red heat.

7.37 Measure the uranium alpha activities by pulsing with a silicon surface-barrier detector and multichannel analyzer.

8.0 CALCULATIONS

8.1 Uranium isotopes on the total filter sample will be determined using the following equation:

$$^{238}\text{U, pCi} = \text{A}\cdot\text{K}\cdot\text{E/D}$$

$$^{235}\text{U, pCi} = \text{B}\cdot\text{K}\cdot\text{E/D}$$

$$^{234}\text{U, pCi} = \text{C}\cdot\text{K}\cdot\text{E/D}$$

where:

A = Net integrated counts of ^{238}U from pulse analysis

B = Net integrated counts of ^{235}U from pulse analysis

C = Net integrated counts of ^{234}U from pulse analysis

D = Net integrated counts of ^{232}U from pulse analysis

E = ^{232}U tracer added (dpm)

K = Conversion factor to pCi = 1 pCi/2.22 dpm.

8.2 Uranium isotopes in air will be determined using the following equation.

$$^{238}\text{U, pCi/m}^3 = \text{A}\cdot\text{K}\cdot\text{E/D}\cdot\text{V}$$

$$^{235}\mathrm{U},\ \mathrm{pCi/m^3} = B \cdot K \cdot E / D \cdot V$$

$$^{234}\mathrm{U},\ \mathrm{pCi/m^3} = C \cdot K \cdot E / D \cdot V$$

where:

V = Volume of air (m^3).

9.0 PRECISION AND ACCURACY

9.1 The precision of this is estimated to be ±15 percent.

9.2 The accuracy has not been established.

10.0 REFERENCES

1. Gindler, J. E., March, 1962. The Radiochemistry of Uranium, NAS-NS 3050.

2. Johns, F. B., Editor, February, 1975. Handbook of Radiochemical Methods, EPA-680/4-75-001.

DETERMINATION OF URANIUM (TOTAL) IN WATER BY FLUOROMETRIC ANALYSIS
(Method EC-191)

1.0 SCOPE AND APPLICATION

1.1 This method is applicable for determining the total uranium content in drinking water, surface and ground waters, and domestic and industrial wastes.

1.2 The lowest reported concentration of total uranium in water, when a 20-mL sample is used, is 0.001 mg/L.

1.3 The highest concentration that can be determined without sample dilution is 0.05 mg/L.

2.0 SUMMARY OF METHOD

2.1 The uranium is extracted into tri-n-octyl-phosphine oxide (TOPO) dissolved in Varsol. (Hexane may be substituted for Varsol.) An aliquot of the organic phase is fused in a flux of anhydrous sodium fluoride containing 2 percent lithium fluoride. The yellow-green uranium fluorescence of the pellet is measured using a fluorophotometer and compared to the fluorescence of a known uranium standard. In an alternate procedure (ASTM Standards, 1976), methyl isobutyl ketone may be used to complex and extract the uranium.

3.0 INTERFERENCES

3.1 Heavy metals may suppress the fluorescence intensity if the uranium is not extracted from the sample prior to analysis.

4.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

4.1 Samples may be collected in 100-mL glass or plastic containers that have been cleaned by rinsing with 1:1 HNO_3.

4.2 The sample may be preserved for up to 6 months by making the $pH < 2$ at collection.

5.0 APPARATUS

5.1 Fluorophotometer - Modified Oak Ridge National Laboratory Model Q-1165 or equivalent.

5.2 Burner - Modified Fletcher; or induction furnace.

5.3 Dishes - Platinum, fusion, 11/16-in. diameter, 1/16-in. lip width, and 1/8-in. deep.

5.4 Dish holder - Aluminum.

5.5 Pelletizer - Delivering a 0.3- or 0.6-g pellet of flux.

5.6 Infrared lamp and stand.

5.7 Mechanical roller.

5.8 Laboratory shaker.

5.9 Pipets - Eppendorf 100- and 200-uL semiautomatic or equivalent.

5.10 Optical pyrometer.

6.0 REAGENTS

6.1 Nitric acid - Concentrated (70 percent).

6.2 Nitric acid (2M) - Add 62.5 mL of concentrated nitric acid to 437.5 mL of distilled water in a 500-mL polyethylene wash bottle and mix thoroughly.

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6.3 Sodium fluoride - 2 percent lithium fluoride flux. Put 1359 g (3 lb) of fluorometric grade sodium fluoride and 27 g of lithium fluoride into a clean 5-lb glass reagent jar. Place the jar on the mechanical roller and roll for 48 h.

6.3.1 Alternate flux - Sodium fluoride. The lithium fluoride additive is unnecessary when fusion is accomplished by induction heat.

6.4 Tri-n-octyl-phosphine oxide (TOPO) dissolved in Varsol, 0.05 M - (Hexane may be substituted for Varsol.) Dissolve 100 g of tri-n-octyl-phosphine oxide in 1500 mL of Varsol in a 2000-mL beaker. Filter the solution through fluted filter paper into a 2-gal polyethylene bottle. Add sufficient volume to make a total volume of 5 L, and mix thoroughly.

6.5 Stock uranium solution - Dissolve 117.9 mg of natural U_3O_8 in 8 M HNO_3 in 100-mL beaker. Transfer the solution to a 100-mL flask using 2 M HNO_3 to transfer. Dilute to volume with distilled water. Mix thoroughly. 1 mL = 1 mg U or 1 g/L.

6.6 Control Standard No. 1 - Transfer 10 mL of stock solution to a 1-L flask and dilute to volume with 2 M HNO_3. Mix thoroughly. 1 mL = 10 g U or 10 mg/L.

6.7 Control Standard No. 2 - Transfer 2 ml of control solution No. 1 to a 1-L flask and dilute to volume with 2 M HNO_3. Mix thoroughly. 1 mL = 0.02 ung U or 0.02 mg/L.

6.8 Control Standard No. 3 - Transfer 50 mL of control solution No. 2 to a 1-L flask and dilute the volume with 2 M HNO_3. Mix thoroughly. 1 mL = 1.0 ng U or 0.001 mg/L.

7.0 PROCEDURE

7.1 Pipet 20 mL of sample (or standard) into a 50-mL glass vial, add 3 mL of concentrated nitric acid, and swirl to mix.

7.2 Add 2 mL of TOPO solution, put cap on vial, place vial on laboratory shaker, and shake for 10 min.

7.3 Process a blank and standards of 0.001 mg and 0.02 mg uranium/L along with the sample.

7.4 Remove the vials from the shaker and allow the solutions to stand 1 min for the organic and aqueous layers to separate.

7.5 With the pelletizer, place a 0.3- or 0.6-g pellet of the fluoride flux into each platinum fusion dish to be used.

7.6 Fusion using a modified Fletcher Burner.

7.6.1 Place the platinum dishes on a nichrome screen.

7.6.2 Pipet 100 or 200 uL of organic layer from Section 7.4 onto each pellet, using the appropriate Eppendorf pipet.

7.6.3 Place the screen under an infrared heat lamp and allow the samples to dry for 30 min. The lamp shall be approximately 6 in. above the samples.

7.6.4 Remove the screen from under the lamp and put it over the fusion burner; fuse for 2 min at approximately 1100°C, then reduce to 950°C and fuse for 1 min. (An optical pyrometer will provide temperature estimates.)

7.6.5 Remove the screen containing the dishes from the burner and allow to cool.

7.7 Fusion using an induction furnace.

7.7.1 Pipet 200 uL of organic layer from Section 7.4 onto each pellet, using the Eppendorf pipet.

7.7.2 Place the holder under an infrared heat lamp and allow the samples to dry for 30 min. The lamp shall be approximately 6 in. above the pellets.

7.7.3 Remove the holder from under the lamp and place four dishes at a time in the induction furnace coil.

7.7.4 Apply 600 ma current for 60 s.

7.7.5 Transfer the dishes back to the holder to cool. (Caution: Use forceps.)

7.8 Place the platinum dishes containing the blank, uranium standards, and sample melts on the turn-table of the fluorophotometer.

7.9 Move the blank under the ultraviolet light and adjust the zero control knob to make the instrument read zero. Remove the blank.

7.10 Move the 0.02 mg/L standard melt under the ultraviolet light and adjust the calibration control until the instrument reads the known value of the standard. Remove the standard.

7.11 Move the 0.001-mg/L uranium standard melt under the ultraviolet light. The known value of the standard will be read if the instrument is properly calibrated (Section 7.10). Remove the standard. The fluorophotometer is now calibrated for direct readout of uranium concentrations from 0.001 through 0.02 mg/L.

7.12 Move the sample pellets under the ultraviolet light of the fluorophotometer and read the uranium concentration of the samples. Record the readings in mg U/L.

8.0 CALCULATION

8.1 Multiply the reading on the sample by the appropriate dilution factor to determine concentration on the sample basis.

$$\text{Uranium (mg/L)} = R \times D$$

where:

R = Reading
D = Dilution factor.

8.2 If the fluorophotometer used does not have a direct concentration readout capability, meter readings of fluorescence intensity of standards can be used to plot a calibration curve. Intensity readings from samples are then compared to the calibration curve to obtain sample concentrations in mg U/L.

9.0 PRECISION AND ACCURACY

9.1 Measurements were made on 69 water samples, each containing 0.005 mg U/L by this method with a relative standard deviation of ±5 percent and a recovery of 98.3 percent.

10.0 REFERENCES

1. Centanni, F. A., A. M. Moss, and M. A. DeSesse, 1956. "Fluorometric Determination of Uranium," Anal. Chem., 28, p. 1651.

2. ASTM Standards, 1976. Part 31, p. 700, Method D 2907-75.

DETERMINATION OF URANIUM IN WATER

1.0 SCOPE AND APPLICATION

1.1 This general method covers the determination of uranium in water samples. It has been used to evaluate the possible contamination of waters near nuclear facility sites. Waters containing <1 to >1000 ppm of uranium have been analyzed.

1.2 The fluorescence of the inorganic uranyl salts has been known for a long time and is the basis of the conventional fluorimetric analytical method (1). The procedure described here is more rapid, less susceptible to interferences and ten times more sensitive than the conventional method. The lower limit is 0.05 ppb U(2, 3, 4).

1.3 The Scintrex UA-3 Uranium Analyzer contains a nitrogen laser-emitting ultraviolet radiation of 337 nm as an excitation source. Under ultraviolet excitation, uranyl salts emit a green radiation, and the intensity is measured using a photomultiplier tube.

1.4 The criterion for compatibility for a sample with UA-3 measurement is that the uranium be in aqueous solution near neutrality with relatively little suspended matter and free of large amounts of organic materials. The acid concentration in the final solution to be analyzed should not exceed 0.1 percent for the Fluran buffer to be effective.

2.0 SUMMARY OF METHOD

2.1 Water samples preserved when collected in the field with NHO_3 to pH <2 generally do not require any treatment before analysis. The fluorescence of the uranyl ion produced by pulsed-laser radiation in the ultraviolet is enhanced by the addition of a reagent called "Fluran" (a proprietary pyrophosphate reagent of the Scintrex Company). A Scintrex UA-3 Uranium analyzer is used to measure the fluorescence differentially; i.e., readings are taken before and after the addition of Fluran and the concentration of uranium is determined using the standard addition technique. The electronic system of the UA-3 analyzer is gated to accept signals from the photodetector after the fluorescence from any organic species has decayed to zero.

3.0 INTERFERENCES

3.1 As in other fluorimetric techniques, several interfering species exist which either enhance or quench the fluorescence.

3.2 Some interferences include Fe, Mn, Ca, Mg, Ag, Th, and Sr in the 100- to 1000-ppm range. The quenching effect, for a given concentration of the interfering species, depends on the photochemistry of the particular uranyl complex involved.

3.3 The anions, NO_3^-, Cl^-, $SO_4^=$, and $CO_3^=$ are quenchers. Their concentration can be controlled in the sample preparation. Note: Sample solutions that are too acidic can be neutralized by adding NaOH.

3.4 Organic material (humic substances) fluoresce. In this procedure, the bulk of this material can be destroyed by ignition if necessary. This interference is also minimized by the difference in the "lifetimes" of uranyl fluorescence and those of organic compounds in solution. However, by using the standard addition technique, most sample matrix effects are overcome.

4.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

4.1 Generally, no preparation of water is required. Note that aliquots taken for analysis must be free of suspended matter. Therefore, in place of filtering the insoluble material (if present) allow it to settle by gravity overnight so that the solution is clear.

4.2 The requestor may specify in the Request for Analysis the number of standard samples and the relative standard deviation of results on these samples needed for the desired level of confidence. Otherwise, three standard aliquots will be run each day (see Section 7.1.8) to achieve a relative standard deviation indicated in the precision and accuracy requirements.

5.0 APPARATUS AND EQUIPMENT

5.1 Scintrex UA-3 Uranium Analyzer.

5.2 Rectangular 20 x 10 mm quartz fluorescence cell - 7-mL capacity.

5.3 Magnetic stirrer.

5.4 TFE-fluorocarbon-coated stirring bar - Sargent-Welch Scientific Company, Catalog No. S-76507-90, is this type.

5.5 Bottle-top Dispensers - 2 to 10 mL and 1 to 5 mL.

5.6 Volumetric flasks - Assorted sizes dedicated to low-level uranium use. Clean by rinsing with water generously, then adding 5 mL concentrated HCl, soaking, and finally rinsing generously with water. Labware can be checked by running blanks.

5.7 Aspiration devise - A 1-L plastic bottle attached to the lab vacuum for waste solution collection.

6.0 REAGENTS

6.1 Acids, Concentrated - HNO_3, HCl. Note: Reagent-grade chemicals, ACS or equivalent shall be used.

6.2 Fluran - Trade name of a pyrophosphate fluorescence reagent obtained from the Scintrex Company.

6.3 Uranium standard stock solution - Dissolve 118 mg freshly ignited SRM 950b U_3O_8 (or equivalent) in 5 mL HNO_3. Dilute to 100 mL (1.0 mg U/mL).

6.4 Uranium Standard Dilution 1 - Pipet 1000 uL of the Uranium standard stock solution into a 100-mL volumetric flask. Add 2 mL concentrated HNO_3 and dilute to volume (10.0 ug U/mL).

6.5 Uranium Standard Dilution 2 - Pipet 250 uL of Uranium Standard Dilution 1 into a 25-mL volumetric flask. Add 100 L concentrated HNO_3 and dilute to volume. This solution should be prepared fresh daily (0.10 ug U/mL).

7.0 PROCEDURE

7.1 Instrument Setup

7.1.1 Switch power to ON.

7.1.2 Approximately 4 min after the power is switched on, the LASER READY indicator will light up. Then the laser can be switched on. Let stabilize 15 to 30 min after switching on. Keep the laser on during an entire running session during any particular day.

7.1.3 Set the RANGE switch to LOW. The UA-3 instrument has a low and HIGH range position. It will probably be used with the switch in the LOW range for a nominal 10 ng U full-scale meter deflection. The HIGH range selects a X10 attenuator to allow a nominal range up to 75 ng with sensitivity set at 510.

7.1.4 Set the SENSITIVITY switch according to need, typically at 510. The sensitivity can be varied to accommodate solutions of diverse uranium concentrations.

7.1.5 Turn the photomultiplier (PMT) switch to ON. This switch shall be turned on only after the sample door is closed and the handle returned to an upright position. The photomultiplier tube with high voltage applied will be damaged by ambient light. The instrument has a mechanical interlock to prevent this from occurring.

7.1.6 Zero the meter using the ZERO control. Adjustments are made as a series of steps rather than as a continuous movement because the instrument displays an integrated reading every 4 sec.

7.1.7 Press the button for LASER INTENSITY and record the reading. Daily records of the laser output shall be kept. Because the laser tube/thyratron assembly has a limited lifetime, its output is expected to diminish over time, and replacement is required when its output has become either too low or too erratic for useful analytical results.

7.1.8 Aliquots of Uranium Standard Dilution 2 shall be run each day. Aliquots of uranium concentration to span the range of interest shall be taken. Follow sample measurement in Section 7.2.

7.2 Sample Measurement

7.2.1 Add 5.0 mL of deionized water from the dispenser bottle to the cuvette containing the Teflon stirring bar. Always hold the cell by its top corners only--avoid leaving fingerprints on the faces of the cell. "Polish" cell windows with lint-free paper.

7.2.2 Add a sample aliquot, typically 0.01 to 1.0 mL, to the cell. If a larger sample aliquot than 1 mL is taken, the amount of water added in Section 7.2.1 shall be adjusted so that the total volume in the cell at this point is no more than 6.0 mL. Samples high in uranium or interferences can be diluted. The dilutions should be made 1 percent in either HNO_3 or HCL.

7.2.3 Mix on the magnetic stirrer for 30 sec.

7.2.4 Insert the cell into the fluorometer.

7.2.5 Switch the PMT on. Remember the door must be closed.

7.2.6 Adjust the instrument meter to zero with the BALANCE control to compensate for any residual fluorescence not due to uranium. If the instrument cannot be balanced, so much uranium may be present in the sample as to yield appreciable fluorescence even before Fluran is added. Discard the solution and try a smaller aliquot.

7.2.7 Switch the PMT off.

7.2.8 Add 1.0 mL of Fluran from the dispenser bottle to the cell. If the Fluran reacts with the sample to form a precipitate, the meter readings are invalid. Try a smaller aliquot or another dilution or filter the sample solution. The primary function of the Fluran is the formation of a single fluorescent uranyl species. It also acts as a strong complexing agent for other metals in solution to reduce their effects on uranyl luminescence. The Fluran contains a buffer to maintain optimum pH for both luminescence and masking efficiency.

7.2.9 Mix on the magnetic stirrer for 30 s.

7.2.10 Insert the cell in the fluorometer. The data reading can be done automatically by using the interface box and the computer menu stored in CMTVAX. If automatic data collection is desired, switch on the interface box power to ON (leave ON all day) and also switch the data collection toggle ON so that the appropriate reading will be fed directly into the computer.

7.2.11 Switch the PMT on.

7.2.12 Record the fluorescence reading of the third and fourth integrations either manually or automatically. An overload light indicates that the concentration of a sample is such that full scale deflection is exceeded by a factor of 3. Switching to the HIGH range may give a reading. A sample left in the fluorometer will steadily decline in fluorescence over a period of several seconds because the lifetime of uranyl fluorescence is temperature dependent and the cell cavity is usually slightly warmer than the ambient temperature.

7.2.13 Switch the PMT off.

7.2.14 Add an aliquot of uranium standard solution to the cell using the following guideline.

Sample Reading	Add	uL of U Std. Dil. 2
0-0.5	5 ng	50
0.5-1.0	10 ng	100
1.0-2.0	25 ng	250
>2.0	50 ng	500

Note: If these guidelines are followed, it will be necessary to switch to the HIGH range when the initial reading is > 0.6 to be sure the standard addition fluorescence reading is on scale.

7.2.15 Mix on the magnetic stirrer for 30 s.

7.2.16 Insert the cell in the fluorometer.

7.2.17 Switch the PMT on.

7.2.18 Record the fluorescence reading of the third and fourth integrations either manually or automatically.

7.2.19 Switch the PMT off.

7.2.20 Remove the solution from the cell by aspirating into a waste collection bottle. Rinse the cell thoroughly with deionized water before analyzing the next sample. The cell should be filled with deionized water that is aspirated into the waste collection bottle a minimum of five times.

7.3 Instrument Shutdown

7.3.1 Switch the laser off after each day's use to prolong laser life.

7.3.2 Turn the complete system off when the instrument will not be used for several days or more.

8.0 CALCULATION

8.1 Uranium content in water will be determined using the following equation.

$$U(\text{ug/g or ug/mL}) = \frac{S \cdot SP \cdot (W + SA + FL) \cdot R1 \cdot SV}{SW \cdot SA \cdot [(SP + W + SA + FL)(R2) - (W + SA + FL)(R1)]}$$

where:

S = U standard used as the spike (U Std. Dil. 2) (g/mL)

SP = U spike added (mL)

W = H_2O added (mL)

SA = Sample aliquot (mL)

FL = Fluran added (mL)

R1 = Average of Section 7.2.12 readings

SV = 1

SW = 1

R2 = Average of Section 7.2.18 readings.

8.2 When the above calculation is used for the uranium standard, which is a solution, both SV and SW will have a value of 1.0.

8.3 If the computer program is used, this calculation will be followed.

9.0 PRECISION AND ACCURACY

9.1 The relative standard deviation of this method is 2.1 percent. This applies to meter readings between 0.1 and 1.0 and with concentrations of uranium between 0.5 and 2000 ppm. At the

95 percent confidence level, duplicate aliquots of sample solutions are expected to agree within ±4.4 percent.

9.2 At the present time, there is no NBS standard reference water analyzed for uranium. However, analysis of NBS SRM-1648, Urban Particulate Matter, with a uranium certification of 5.5 ± 0.1 ppm, indicated no bias in the method within the precision stated above.

9.3 As further confirmation of the accuracy, the same soil samples were analyzed by the fluorescence method and by mass spectrometric isotopic dilution. The results agreed within the precision stated above.

10.0 REFERENCES

1. Price, G. R., R. J. Ferretti and S. Schwartz, 1953. "Fluorophotometric Determination of Uranium," Anal. Chem. 25 (2), 322-331.

2. Campen, W. and K. Bachmann, 1979. "Laser-Induced Fluorescence for the Direct Determination of Small Concentrations of Uranium in Water," Mikrochimica Acta (Wien) II, 159-170.

3. Scintrex Instructional Manual, UA-3 Uranium Analyzer, Scintrex, Concord, Ontario, Canada, 8-78.

4. Zook, A. C., L. H. Collins and C. E. Pietri, 1981. "Determination of Nanogram Quantities of Uranium by Pulsed-Laser Fluorometry," Mikrochimica Acta (Wien) II, 457-468.

DETERMINATION OF URANIUM IN SOILS, SEDIMENTS, AND SLUDGES

1.0 SCOPE AND APPLICATION

1.1 This general method covers the determination of uranium in soil, sediment, and sludge samples. It has been used to evaluate the possible contamination of soils near nuclear facility sites. Soils containing <1 to >1000 ppm of uranium have been analyzed.

1.2 The fluorescence of the inorganic uranyl salts has been known for a long time and is the basis of the conventional fluorimetric analytical method (1). The procedure described here is more rapid, less susceptible to interferences and ten times more sensitive than the conventional method. The lower limit is 0.05 ppb U(2, 3, 4).

1.3 The Scintrex UA-3 Uranium Analyzer contains a nitrogen laser-emitting ultra-violet radiation of 337 nm as an excitation source. Under ultraviolet excitation, uranyl salts emit a green radiation, and the intensity is measured using a photomultiplier tube.

1.4 The criterion for compatibility for a sample with UA-3 measurement is that the uranium be in aqueous solution near neutrality with relatively little suspended matter and free of large amounts of organic materials. The acid concentration in the final solution to be analyzed should not exceed 0.1 percent for the Fluran buffer to be effective.

2.0 SUMMARY OF METHOD

2.1 The sample is ignited in a muffle furnace to burn off organic material and the uranium is solubilized by acid leaching. The fluorescence of the uranyl ion produced by pulsed laser radiation in the ultraviolet is enhanced by the addition of a reagent called "Fluran" (a proprietary pyrophosphate reagent of the Scintrex

Company). A Scintrex UA-3 Uranium analyzer is used to measure the fluorescence differentially; i.e., readings are taken before and after the addition of Fluran and the concentration of uranium is determined using the standard addition technique. The electronic system of the UA-3 analyzer is gated to accept signals from the photodetector after the fluorescence from any organic species has decayed to zero.

3.0 INTERFERENCES

3.1 As in other fluorimetric techniques, several interfering species exist which either enhance or quench the fluorescence.

3.2 Some interferences include Fe, Mn, Ca, Mg, Ag, Th, and Sr in the 100- to 1000-ppm range. The quenching effect, for a given concentration of the interfering species, depends on the photochemistry of the particular uranyl complex involved.

3.3 The anions, NO_3^-, Cl^-, $SO_4^{=}$, and $CO_3^{=}$ are quenchers. Their conentration can be controlled in the sample preparation. Sample solutions that are too acidic can be neutralized by adding NaOH.

3.4 Organic material (humic substances) fluoresce. In this procedure, the bulk of this material is destroyed by ignition. This interference is also minimized by the difference in the "lifetimes" of uranyl fluorescence and those of organic compounds in solution. However, by using the standard addition technique, most sample matrix effects are overcome.

4.0 APPARATUS AND EQUIPMENT

4.1 Scintrex UA-3 Uranium Analyzer.

4.2 Rectangular 20 x 10 mm quartz fluorescence cell - 7-mL capacity.

4.3 Magnetic stirrer.

4.4 TFE-Fluorocarbon-coated stirring bar - Sargent-Welch Scientific Company, Catalog No. S-76507-90, is this type.

4.5 Bottle-top dispensers - 2-10 mL and 1-5 mL.

4.6 Analytical balance - Readable to 0.0001 g.

4.7 Volumetric flasks - Assorted sizes dedicated to low-level uranium use. Clean by rinsing with water generously, then adding 5 mL concentrated HCl, soaking, and finally rinsing generously with water. Labware can be checked by running blanks.

4.8 Aspiration devise - A 1-L plastic bottle attached to the lab vacuum for waste solution collection.

4.9 Fume hood designed for perchloric acid fuming. A "clean" air hood dedicated to handling low-level uranium samples shall be used.

4.10 Platinum Crucibles - 30 mL size or equivalent.

5.0 REAGENTS

5.1 Acids - Concentrated HNO_3, HCl, $HClO_4$, and HF. Reagent-grade chemicals ACS or equivalent shall be used.

5.2 Fluran - Trade name of a pyrophosphate fluorescence reagent obtained from the Scintrex Company.

5.3 Uranium standard stock solution - Dissolve 118 mg freshly ignited SRM 950b U_3O_8 (or equivalent) in 5 mL HNO_3. Dilute to 100 mL (1.0 mg U/mL).

5.4 Uranium Standard Dilution 1 - Pipet 1000 uL of the uranium standard stock solution into a 100-mL volumetric flask. Add 2 mL concentrated HNO_3 and dilute to volume (10.0 ug U/mL).

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5.5 Uranium Standard Dilution 2 - Pipet 250 uL of Uranium Standard Dilution 1 into a 25-mL volumetric flask. Add 100 uL concentrated HNO_3 and dilute to volume. This solution should be prepared fresh daily (0.10 ug/U/mL).

6.0 PROCEDURE

6.1 Sample Preparation

6.1.1 Accurately weigh 1.0 to 2.0 g (wet weight) portion of representative sample into a tared 30-mL platinum crucible on the four-place balance. It is best to process samples in batches of about 20.

6.1.2 Place the crucible plus sample in a drying oven that is set at 103° to 105°C. Dry the sample to constant weight. (Drying overnight may be convenient.)

6.1.3 Remove from the drying oven and, when cooled, weigh again so that the percent solids can be calculated as follows:

$$\text{Wt. \% Solids} = \frac{\text{g Sample Dry Weight}}{\text{g Sample Wet Weight}} \times 100$$

Calculate so that data can be reported on a dry weight basis.

6.1.4 Place the sample in a cold muffle furnace. Heat to 600°C ± 50°C and keep at this temperature 3 to 4 h. (Overnight may be convenient.)

6.1.5 Transfer the sample to a 100-mL Teflon beaker using deionized water to quantitatively wash it from the crucible intc the beaker.

6.1.6 Add 2 mL of concentrated HF.

6.1.7 Add 2 mL each of concentrated HCl, HNO_3, and $HClO_4$.

6.1.8 Evaporate on a hot plate to dryness in the "clean" perchloric acid fuming hood.

6.1.9 Cool and add 2 mL of concentrated HCl.

6.1.10 Let stand 1/2 to 1 h, swirling three times during this time.

6.1.11 Add 10 mL of deionized water. Swirl.

6.1.12 Heat gently 20 min to dissolve as much residue as possible.

6.1.13 Cool and transfer to 100-mL volumetric flasks.

6.1.14 Dilute to the mark and shake well.

6.1.15 Let stand until the insoluble residue settles to the bottom of the flask and the solution is clear. (Overnight may be convenient.) Filter if, on visual inspection, the insoluble material has not settled.

6.2 Instrument Setup

6.2.1 Switch power to ON.

6.2.2 Approximately 4 min after the power is switched on, the LASER READY indicator will light up. Then the laser can be switched on. Let stabilize 15 to 30 min after switching on. Keep the laser on during an entire running session during any particular day.

6.2.3 Set the RANGE switch to LOW. The UA-3 instrument has a LOW and HIGH range position. It will probably be used with the switch in the LOW range, for a nominal 10 ng U full-scale meter deflection. The HIGH range selects a X10 attenuator to allow a nominal range up to 75 ng with sensitivity set at 510.

6.2.4 Set the SENSITIVITY switch, typically at 510. The sensitivity can be varied to accommodate solutions of diverse uranium concentrations.

6.2.5 Turn the photomultiplier (PMT) switch to ON. This switch shall be turned on only after the sample door is closed and the handle returned to an upright position. The photomultiplier tube with high voltage applied will be damaged by ambient light. The instrument has a mechanical interlock to prevent this from occurring.

6.2.6 Zero the meter using the ZERO control. Adjustments are made as a series of steps rather than as a continuous movement because the instrument displays an integrated reading every 4 s.

6.2.7 Press the button for LASER INTENSITY and record the reading. Daily records of the laser output shall be kept. Because the laser tube/thyratron assembly has a limited lifetime, its output is expected to diminish over time, and replacement is required when its output has become either too low or too erratic for useful analytical results.

6.2.8 Aliquots of Uranium Standard Dilution 2 should be run each day. Aliquots of uranium concentration to span the range of interest should be taken. Follow sample measurement steps in Section 6.3. The requestor may specify in the Request for Analysis the number of standard samples and the relative standard deviation of results on these samples needed for the desired level of confidence. Otherwise, three standard aliquots will be run each day to achieve a relative standard deviation indicated in the precision and accuracy requirements.

6.2.9 A blank shall be taken through the procedure and analyzed with each batch.

6.3 Sample Measurement

6.3.1 Add 5.0 mL of deionized water from the dispenser bottle to the cuvette containing the Teflon stirring bar. Always hold the cell by its top corners only--avoid leaving fingerprints on the faces of the cell. "Polish" cell windows with lint-free paper.

6.3.2 Add a sample aliquot, typically 0.01 to 1.0 mL, to the cell. If a larger sample aliquot than 1 mL is taken, the amount of water added in Section 6.3.1 shall be adjusted so that the total volume in the cell at this point is no more than 6.0 mL.

6.3.3 Mix on the magnetic stirrer for 30 s.

6.3.4 Insert the cell into the fluorometer.

6.3.5 Switch the PMT on. Remember the door must be closed.

6.3.6 Adjust the instrument meter to zero with the BALANCE control to compensate for any residual fluorescence not due to uranium. If the instrument cannot be balanced, so much uranium may be present in the sample as to yield appreciable fluorescence even before Fluran is added. Discard the solution and try a smaller aliquot.

6.3.7 Switch the PMT off.

6.3.8 Add 1.0 mL Fluran from the dispenser bottle to the cell. If the Fluran reacts with the sample to form a precipitate, the meter readings are invalid. Try a smaller aliquot or another dilution or filter the sample solution. The primary function of the Fluran is to form a single fluorescent uranyl species. It also acts as a strong complexing agent for other metals in solution to reduce their effects on uranyl luminescence. The Fluran contains a buffer to maintain optimum pH for both luminescence and masking efficiency.

6.3.9 Mix on the magnetic stirrer for 30 s.

6.3.10 Insert the cell in the fluorometer. The data readings can be done automatically by using the interface box and the computer menu stored in CMTVAX. If automatic data collection is desired, switch the interface box power to ON (leave on all day) and also switch on the data collection toggle so that the appropriate readings will be fed directly into the computer.

6.3.11 Switch the PMT on.

6.3.12 Record the fluorescence reading of the third and fourth integrations either manually or automatically. An overload light indicates that the concentration of a sample is such that full scale deflection is exceeded by a factor of 3. Switching to the High range may give a reading. A sample left in the fluorometer will steadily decline in fluorescence over a period of several seconds because the lifetime of uranyl fluorescence is temperature dependent and the cell cavity is usually slightly warmer than the ambient temperature.

6.3.13 Switch the PMT off.

6.3.14 Add an aliquot of uranium standard solution to the cell using the following guideline.

Sample Reading	Add	uL of U Std. Dil. 2
0-0.5	5 ng	50
0.5-1.0	10 ng	100
1.0-2.0	25 ng	250
>2.0	50 ng	500

Note: If these guidelines are followed, it will be necessary to switch to the high range when the initial reading is >0.6 to be sure the standard addition fluorescence reading is on scale.

6.3.15 Mix on the magnetic stirrer for 30 s.

6.3.16 Insert the cell in the fluorometer.

6.3.17 Switch the PMT on.

6.3.18 Record the fluorescence reading of the third and fourth integrations either manually or automatically.

6.3.19 Switch the PMT off.

6.3.20 Remove the solution from the cell by aspirating into a waste collection bottle. Rinse the cell thoroughly with deionized water before introduction of the next sample for analysis. It should be filled with deionized water that is aspirated into the waste collection bottle a minimum of five times.

6.4 Instrument Shutdown

6.4.1 Switch the laser off after each day's use to prolong laser life.

6.4.2 Turn the complete system off when the instrument will not be used for several days or more.

7.0 CALCULATION

7.1 Calculate the uranium content using the following equation:

$$U\,(\text{ug/g or ug/mL}) = \frac{S \cdot SP \cdot (W + SA + FL) \cdot R1 \cdot SV}{SW \cdot SA \cdot [(SP + W + SA + FL)(R2) - (W + SA + FL)(R1)]}$$

where:

S = U standard used as the spike (U Std. Dil. 2) (ug/mL)

SP = U spike added (mL)

W = H_2O added (mL)

SA = Sample aliquot (mL)

FL = Fluran added (mL)

R1 = Average of Section 6.3.12 readings

SV = Total sample solution (mL)

SW = Weight of dry sample (g) (See Section 6.1.3.)

R2 = Average of Section 6.3.18 readings.

7.2 When the calculation above is used for the uranium standard, which is a solution, both SV and SW will have a value of 1.0.

7.3 If the computer program is used, this calculation will be followed.

8.0 PRECISION AND ACCURACY

8.1 The relative standard deviation is 2.1 percent. This applies to meter readings between 0.1 and 1.0 and with concentrations of uranium between 0.5 and 2000 ppm. At the 95 percent confidence level, duplicate aliquots of sample solutions are expected to agree within ±4.4 percent.

8.2 At the present time, there is no NBS standard reference soil analyzed for uranium. However, analysis of NBS SRM-1648, Urban Particulate Matter, with a uranium certification of 5.5 ± 0.1 ppm, indicated no bias in the method within the precision stated above.

8.3 As further confirmation of the accuracy, the same soil samples were analyzed by the fluorescence method and by mass spectrometric isotopic dilution. The results agreed within the precision stated above.

9.0 REFERENCES

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2. Campen, W. and K. Bachmann, 1979. "Laser-Induced Fluorescence for the Direct Determination of Small Concentrations of Uranium in Water," Mikrochimica Acta (Wien) II, 159-170.

3. Scintrex Instructional Manual, UA-3 Uranium Analyzer, Scintrex, Concord, Ontario, Canada, 8-78.

4. Zook, A. C., L. H. Collins and C. E. Pietri, 1981. "Determination of Nanogram Quantities of Uranium by Pulsed-Laser Fluorometry," Mikrochimica Acta (Wien) II, 457-468.

DETERMINATION OF THORIUM (ALPHA-EMITTING) ISOTOPES IN WATER

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the determination of the isotopes of thorium in potable, natural, and industrial waters.

1.2 At Oak Ridge National Laboratory (ORNL), the lowest concentration reported is 4 x 10 pCi/mL when analyzing a 1-L sample, counting for 1000 min on an alpha pulse-height analyzer with a detector having a 20 percent efficiency and a 0.005-cpm background over each energy region of interest, and realizing an 80 percent chemical recovery of the thorium.

1.3 At other Union Carbide Corporation - Nuclear Division (UCC-ND) plants, the lowest reported concentration is 4 x 10^4 pCi/mL for 1 L samples.

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0 SUMMARY OF METHOD

2.1 Thorium-234 tracer (an alpha emitter) is equilibrated with the thorium isotopes in the sample.

2.2 All of the thorium isotopes are coprecipitated with praseodymium as the hydroxide and the fluoride.

2.3 The thorium is finally purified by extracting with thenoyltrifluoroacetone (TTA)-xylene.

2.4 The TTA extract is dried on a stainless steel disc; the chemical yield is determined by evaluating the recovered ^{234}Th by beta counting.

2.5 The alpha-emitting thorium isotopes are determined by alpha pulse-height analysis.

3.0 INTERFERENCES

3.1 This method does not separate uranium adequately when the uranium/thorium activity ratio is greater than 1. Several of the isotopes of uranium and thorium have alpha energies sufficiently close to cause interferences in pulse-height analysis. Further purification procedures are recommended when the uranium/thorium ratio is known to be greater than 1.

4.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

4.1 If suspended or soluble thorium determinations are separately desired, the samples should first be filtered to remove the suspended particulates as soon as practicable; then the samples should immediately be adjusted to pH 1 with nitric acid.

4.2 If total thorium determinations are desired, the samples should be adjusted to pH 1 with nitric acid, as soon as practicable without filtering.

4.3 After pH adjustments, the samples are stored in glass or plastic containers.

5.0 APPARATUS AND EQUIPMENT

5.1 Vortex mixer.

5.2 Hot plate.

5.3 Centrifuge - Equipped with head for 50 and 100 mL centrifuge tubes.

5.4 Extraction vials - 50 mL, with plastic-lined screw caps.

5.5 Transfer pipets.

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5.6 Beakers - Adequately sized to accommodate the sample aliquot.

5.7 pH Meter - With combination electrode.

5.8 Stainless steel discs - Sized to be compatible with counting equipment.

5.9 Multichannel analyzer system - With silicon surface-barrier detector(s).

5.10 Beta counter - Adequate to accommodate the stainless-steel discs.

5.11 Plastic centrifuge tubes - 50 and 100 mL.

5.12 Water bath.

6.0 REAGENTS

6.1 Praseodymium solution (5 mg/mL) - Dissolve 6.00 g of $Pr(NO_3)_3.6H_2O$ in dilute (2 M) HNO_3 and dilute to 500 mL with water.

6.2 Ammonium hydroxide - Concentrated.

6.3 Potassium dichromate (0.4 M) - Dissolve 11.8 g of $K_2Cr_2O_7$ in water and dilute to 100 mL.

6.4 Hydrofluoric acid - Concentrated.

6.5 Aluminum nitrate solution (2 M) - Dissolve 75.0 g of $Al(NO_3)_3 \cdot 9H_2O$ in water and dilute to 100 mL.

6.6 Nitric acid - Concentrated.

6.7 Nitric acid (1 M) - Dilute 6.25 mL of concentrated HNO_3 to 100 mL with water.

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6.8 Nitric acid solution (pH 1.5) - Transfer 500 mL of water to an 800-mL beaker. Immerse the pH electrode, stir, and adjust the pH to 1.5 with concentrated HNO_3.

6.9 TTA-xylene solution (0.5 M TTA) - Dissolve 55.5 g of TTA (thenoyltrifluoroacetone) in xylene and dilute to 500 mL with xylene.

6.10 Thorium tracer (^{234}Th) - Dissolve 1 g of isotopically depleted U_3O_8 in dilute nitric acid and convert to the chloride by boiling down several times with concentrated HCl, then taking the residue to dryness. Dissolve the uranium chloride in 8 M HCl and extract the uranium with 20 percent (w/v) Adogen 364 in xylene. Retain the aqueous phase for the thorium tracer. Count for ^{234}Th beta activity.

6.11 Ammonium hydroxide, dilute - Dilute 35 mL of concentrated NH_4OH to 500 mL with water.

6.12 Hydrofluoric acid, nitric acid solution, 1 M HF - 1 M HNO_3. Mark a polyethylene bottle at the 100-mL volume level. Add 75 mL of water to the bottle. Using a plastic pipet, add 4 mL of concentrated HF; add 6.25 mL of concentrated HNO_3; dilute to the 100-mL mark with water.

6.13 Adogen 364-xylene solution, 20 percent (w/v) - Weigh 20 g of Adogen 364 (or equivalent) and dilute to 100 mL with xylene.

7.0 PROCEDURE

7.1 Transfer a measured aliquot of the sample to an adequate-sized beaker, check the pH, and, if necessary, add nitric acid to adjust the pH to 1.

7.2 Add 5000 to 10,000 cpm of thorium-234 tracer and 1 mL of praseodymium solution.

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7.3 Place the beaker on a hot plate and allow the sample to heat to near boiling.

7.4 Remove the sample from the hot plate and allow it to cool.

7.5 Add concentrated ammonium hydroxide, while stirring, to a pH of 9.

7.6 Stir the sample sufficiently to induce coalescence of the precipitate, and allow the precipitate to settle (preferably overnight).

7.7 Decant the supernatant solution and quantitatively transfer the precipitate to a 50- or 100-mL centrifuge tube.

7.8 Centrifuge at 2000 rpm for about 10 min.

7.9 Discard the supernatant solution.

7.10 Wash the precipitate with water, centrifuge, and discard the water wash solution.

7.11 Dissolve the precipitate with 8 to 10 drops of concentrated nitric acid.

7.12 Add approximately 0.3 mL of 0.4 M potassium dichromate.

7.13 Digest in a hot water bath that is at or near the boiling point for 10 min.

7.14 Remove from the bath and add approximately 0.3 mL of concentrated hydrofluoric acid. Mix well and allow to digest at room temperature for 10 min.

7.15 Centrifuge at 2000 rpm for 5 min.

7.16 Add two drops of praseodymium solution and swirl gently without disturbing the precipitate.

7.17 Repeat the step in Section 7.15.

7.18 Discard the supernatant solution.

7.19 Wash the precipitate with approximately 2 mL of 1 M HF - 1 M HNO_3 solution that contains three drops of 0.4 M potassium dichromate.

7.20 Repeat the steps in Sections 7.15 and 7.18.

7.21 Dissolve the fluoride precipitate with 0.5 mL of 2 M aluminum nitrate and 5 drops of 1 M HNO_3.

7.22 Transfer the solution to a 50-mL vial.

7.23 Rinse the centrifuge tube with 5 mL of distilled water and add the rinse solution to the 50-mL vial.

7.24 With the aid of the pH meter, adjust the pH of the solution to 1.4 to 1.5 with dilute ammonium hydroxide and/or dilute nitric acid.

7.25 Add 2 mL of 0.5 M TTA-xylene.

7.26 Mix on the Vortex mixer for 10 min.

7.27 Centrifuge at 2000 rpm for about 5 min.

7.28 Transfer the upper phase (TTA-xylene) to a new vial.

7.29 Repeat the steps in Sections 7.25 through 7.28 with the centrifuge tube, transferring the second TTA extract to the same vial.

7.30 Scrub the TTA extract with 5 mL of pH 1.5 nitric acid solution.

7.31 Repeat the step in Section 7.27 and discard the scrub solution.

7.32 Evaporate the entire TTA extract on a stainless steel disc, adding portions in small increments. Flame the disc to a red heat.

7.33 Take an aliquot of ^{234}Th tracer identical with that used in Section 7.2. Evaporate it on a stainless-steel counting disc, adding portions in small increments, to provide a comparator disc. Flame the disc to a red heat.

7.34 Count the sample disc and the ^{234}Th comparator disc on a beta counter. Ratio the sample net beta count to the comparator net beta count to determine the fraction of thorium recovery.

7.35 Perform an alpha pulse-height analysis to determine the identity and quantity of the thorium isotopes present in the sample.

CALCULATIONS

$$\text{Thorium-x (pCi/mL)} = A/B \cdot C \cdot D \cdot V$$

where:

x = Isotope of interest

A = Net integrated count rate (cpm) of thorium-x from the pulse-height analysis

B = Efficiency factor of the alpha pulse-height analyzer system (cpm/dpm)

C = Conversion factor: 2.22 dpm/pCi

D = Fraction of ^{234}Th recovered

V = Volume of the sample (mL).

9.0 PRECISION AND ACCURACY

9.1 The relative precision is estimated to be 20 percent at the 95 percent confidence level.

9.2 The accuracy of this method has not been established; however, repeated determinations on solutions of known concentrations do not indicate a significant bias.

10.0 REFERENCE

1. Moore, F.L., "Radiochemical Determination of Ionium in Uranium Fluorination Ash," Analytical Chemistry, 30, 1958, p. 1020.

DETERMINATION OF THORIUM (ALPHA-EMITTING) ISOTOPES IN SEDIMENT AND SOIL
(Method EC-365)

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to determine the presence of isotopes of thorium in sediment and soil samples.

1.2 At Oak Ridge National Laboratory (ORNL), the lowest reported concentration of thorium isotopes in sediment and soil is 4×10^{-3} pCi/g when analyzing a 10-g sample, realizing a 75 percent chemical recovery of the thorium, and counting for 1000 min on an alpha pulse-height analyzer with a detector having a 20 percent efficiency and a 0.005-cpm background over each energy region of interest.

1.3 At other UCC-ND plants, the lowest concentration reported is 4×10^{-2} pCi/g for a 10-g sample.

2.0 SUMMARY OF METHOD

2.1 The available thorium is leached from the sample material with hot nitric acid and hot nitric acid-hydrogen peroxide treatment.

2.2 The leaching solution is equilibrated with ^{234}Th tracer (an alpha emitter) and passed through anion exchange resin to adsorb the thorium, which is then preferentially eluted with strong hydrochloric acid.

2.3 The thorium is coprecipitated with praseodymium, as the hydroxide and then the fluoride.

2.4 Thorium is then separated from the praseodymium and other rare earths and further purified, by extracting with thenoyltrifluoroacetone (TTA)-xylene.

2.5 The TTA extract is dried on a stainless steel disc, and the chemical recovery is determined by the ^{234}Th tracer.

2.6 The alpha-emitting thorium isotopes are determined by alpha pulse-height analysis.

3.0 INTERFERENCES

3.1 This method does not separate uranium adequately when the uranium to thorium activity ratio is greater than 10. Several of the isotopes of uranium and thorium have alpha energies sufficiently close to cause interferences in pulse-height analysis. Further purification procedures are recommended for thorium when the uranium/thorium ratio is suspected to be greater than 10.

4.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

4.1 The sample materials are oven-dried to a constant weight at 105°C, pulverized, screened to 100-mesh particle size, and thoroughly blended.

4.2 The prepared sample materials are stored in airtight glass or plastic containers.

5.0 APPARATUS AND EQUIPMENT

5.1 Vortex mixer.

5.2 Hot plate.

5.3 Centrifuge.

5.4 Extraction vials - 50 mL with plastic-lined screw caps.

5.5 Transfer pipets.

5.6 Beakers - 500 mL tall-form and 250 mL.

5.7 pH meter with combination electrode.

5.8 Stainless steel discs - Sized to be compatible with counting equipment.

5.9 Multichannel analyzer system with silicon surface-barrier detector(s).

5.10 Beta counter - Adequate to accommodate the stainless steel discs.

5.11 Plastic centrifuge tubes - 50 mL and 100 mL.

5.12 Water bath.

5.13 Magnetic stirring bar - Teflon-coated, 1.5-in. long.

5.14 Analytical balance.

5.15 Muffle furnace - Capable of control at 500°C.

5.16 Ion-exchange column - Glass, 8-mm I.D. by 25-cm long, fitted with a stopcock and reservoir.

5.17 Drying oven, 105°C.

5.18 Screens, 40 and 100 mesh.

6.0 REAGENTS

6.1 Praseodymium solution (5 mg/mL) - Dissolve 6.00 g $Pr(NO_3)_3 \cdot 6H_2O$ in dilute (2 M) HNO and dilute to 500 mL with water.

6.2 Ammonium hydroxide - Concentrated.

6.3 Potassium dichromate (0.4 M) - Dissolve 11.8 g of $K_2Cr_2O_7$ in water and dilute to 100 mL.

6.4 Hydrofluoric acid - Concentrated.

6.5 Aluminum nitrate solution (2 M) - Dissolve 7.50 g of $Al(NO_3)_3 \cdot 9H_2O$ in water and and dilute to 100 mL.

6.6 Nitric acid - Concentrated.

6.7 Nitric acid (1 M) - Dilute 6.25 mL of concentrated HNO_3 to 100 mL with water.

6.8 Nitric acid solution (pH 1.5) - Transfer 500 mL of water to an 800 mL beaker. Immerse the pH electrode, stir, and adjust the pH to 1.5 with concentrated HNO_3.

6.9 TTA-xylene solution (0.5 M TTA) - Dissolve 55.5 g of TTA (thenoyltrifluoroacetone) in xylene and dilute to 500 mL with xylene.

6.10 Thorium tracer (^{234}Th) - Dissolve 1 g of isotopically depleted U_3O_8 in dilute nitric acid and convert to the chloride by boiling down several times with concentrated HCl, then taking the residue to dryness. Dissolve the uranium chloride in 8 M HCl and extract the uranium with 20 percent (w/v) Adogen 364 in xylene. Retain the aqueous phase for the thorium tracer. Take the solution to dryness on a hot plate and convert to the nitrate by boiling down several times with concentrated HNO_3. Take up the Th tracer in 10 mL of 8 M HNO_3 and determine the ^{234}Th beta activity. Isotopically depleted U_3O_8 is used in this preparation because it is quite free from ^{230}Th, an alpha-emitter which would interfere in the measurement.

6.11 Ammonium hydroxide (dilute) - Dilute 35 mL of concentrated NH_4OH to 500 mL with water.

6.12 Hydrofluoric acid-nitric acid solution (1 M HF + 1 M HNO_3, Mark a polyethylene bottle at the 100 mL volume level. Add 75 mL of water to the bottle. Using a plastic pipet, add 4 mL of concentrated HF; add 6.25 mL of concentrated HNO_3; dilute to the 100 mL mark with water.

6.13 Hydrochloric acid - Concentrated.

6.14 Anion-exchange resin - Dowex 1-X4 (50 to 100 mesh, chloride form), or equivalent.

6.15 Hydrochloric acid (8 M) - Add 666 mL of concentrated HCl to 334 mL of water.

6.16 Adogen 364-xylene solution (20 percent w/v) - Weigh 20 g of Adogen 364 (or equivalent) and dilute to 100 mL with xylene.

6.17 Hydrogen peroxide, 30 percent H_2O_2.

6.18 Sodium nitrite, $NaNO_2$ crystals.

7.0 PROCEDURE

7.1 Transfer a measured weight (5 to 10 g) of the 100-mesh sample to a 500-mL tall-form beaker. If the sample shows signs of containing organic matter, ash in a muffle furnace at 500°C for several hours before continuing.

7.2 Slowly add 50 to 75 mL of 8 M HNO_3 and allow sufficient time for any foaming to subside.

7.3 Add 5,000 to 10,000 cpm of thorium-234 tracer.

7.4 Carefully introduce the magnetic stirring bar, place on the hot plate, and digest with stirring at 90° to 95°C for 1 h.

7.5 Remove from the hot plate and transfer the sample solution to a 100-mL plastic centrifuge tube.

7.6 Centrifuge for 10 min at 1500 rpm.

7.7 Decant the supernatant liquid into a 250-mL beaker and retain.

7.8 Rinse the residue from the centrifuge tube into the original 500 mL beaker with 50 to 75 mL of 8 M HNO_3.

7.9 Return to the hot plate and digest with stirring at 90 to 95°C for 1 hr, with the addition of a few drops of 30 percent hydrogen peroxide intermittently for a total of 5 to 10 mL.

7.10 Repeat Sections 7.5 through 7.7.

7.11 Repeat Section 7.8 using 25 mL of 1 M HNO_3.

7.12 Repeat Section 7.9 and 7.10 and discard the residue.

7.13 Add 250 mg of $NaNO_2$ crystals to the combined leachates, place on a hot plate, and bring to a boil rapidly, immediately remove from the heat, and allow the sample to digest for 20 min.

7.14 While the sample is digesting, prepare an anion exchange resin column as follows:

  7.14.1 Place a glass-wool plug in the bottom of the column described in Section 5.16.

  7.14.2 Slurry the resin (see Section 6.14) with water and immediately discard the fines by decanting. Repeat as necessary until fines are removed.

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7.14.3 Transfer 4 mL of resin to the column with water. Prevent any channeling by maintaining the solution level above the resin by use of the stopcock.

7.14.4 Place a glass-wool plug on top of the resin.

7.14.5 Convert the resin to the nitrate form by passing several column volumes of 8 M HNO_3 through the column until the resin is free of chloride ions.

7.15 Transfer the sample solution, cooled to room temperature, to the prepared resin column.

7.16 Place a waste container beneath the column and allow the sample effluent to drain into the waste container at a flow rate of 2 mL/min.

7.17 Rinse the sample beaker with 25 mL of 8 M HNO_3 and transfer the rinse to the column.

7.18 Allow the rinse to drain into the waste container also, and discard the column-effluent waste solution.

7.19 Place a new 250-mL beaker under the column.

7.20 Add 25 ml of 8 M HCl to the column, adjust the flow to 2 mL/min, and retain the column effluent.

7.21 Repeat Section 7.20.

7.22 Add 1 mL of praseodymium solution to the beaker containing the column effluent from Sections 7.20 and 7.21, and mix.

7.23 Place the beaker on a hot plate and reduce the volume to approximately 10 mL. Remove the beaker from the hot plate.

7.24 Add concentrated ammonium hydroxide slowly with stirring to a pH of 9.

7.25 Stir the sample frequently, and allow the precipitate to settle.

7.26 Decant the supernatant solution, and transfer the precipitate to a 50- or 100-mL plastic centrifuge tube.

7.27 Centrifuge at 2000 rpm for about 10 min.

7.28 Discard the supernatant solution.

7.29 Wash the precipitate with water, centrifuge, and discard the water wash solution.

7.30 Dissolve the precipitate with 8 to 10 drops of concentrated nitric acid.

7.31 Add approximately 0.3 mL of 0.4 M potassium dichromate.

7.32 Digest in a boiling hot water bath for 10 min.

7.33 Remove from the bath and add approximately 0.3 mL of concentrated hydrofluoric acid. Mix well and allow to digest at room temperature for 10 min.

7.34 Centrifuge at 2000 rpm for 5 min.

7.35 Add two drops of praseodymium solution and swirl gently without disturbing the precipitate.

7.36 Repeat Section 7.34.

7.37 Discard the supernatant solution.

7.38 Wash the precipitate with approximately 2 mL of 1 M HF - 1 M HNO_3 solution that contains 3 drops of 0.4 M potassium dichromate.

7.39 Repeat Sections 7.34 and 7.37.

7.40 Dissolve the fluoride precipitate with 0.5 mL of 2 M aluminum nitrate and 5 drops of 1 M HNO_3.

7.41 Transfer the solution to a 50-mL vial.

7.42 Rinse the centrifuge tube with 5 mL of distilled water and add the rinse solution to the 50-mL vial.

7.43 With the aid of the pH meter, adjust the pH of the solution to between 1.4 and 1.5 with dilute ammonium hydroxide and/or dilute nitric acid.

7.44 Add 2 mL of 0.5 M TTA-xylene.

7.45 Mix on the Vortex mixer for 10 min.

7.46 Centrifuge at 2000 rpm for about 5 min.

7.47 Transfer the upper phase (TTA-xylene) to a new vial.

7.48 Repeat Sections 7.44 through 7.47 with the centrifuge tube, transferring the second TTA extract to the same vial.

7.49 Scrub the TTA extract with 5 mL of pH 1.5 nitric acid solution.

7.50 Repeat Section 7.46 and discard the scrub solution.

7.51 Evaporate the entire TTA extract on a stainless steel disc, adding portions in small increments. Flame the disc to a red heat.

7.52 Take an aliquot of ^{234}Th tracer identical to that used in Section 7.3. Evaporate it on a stainless steel counting disc, adding portions in small increments, to provide a comparator disc. Flame the disc to a red heat.

7.53 Count the sample disc and the ^{234}Th comparator disc on a beta counter. Divide the sample net count by the comparator net count to determine the fraction of thorium recovery.

7.54 Perform an alpha pulse-height analysis to determine the identity and quantity of the thorium isotopes present in the sample.

8.0 CALCULATIONS

Thorium isotopes will be calculated using the following equation.

$$\text{Thorium-x (pCi/g)} = A/(B \cdot C \cdot D \cdot V)$$

where:

x = Isotope of interest

A = The net integrated count rate (cpm) of thorium-x from the pulse-height analysis

B = The efficiency factor of the alpha pulse-height analyzer system (cpm/dpm)

C = The conversion factor (2.22 dpm/pCi)

D = The fraction of ^{234}Th recovered

V = Weight of sample (g).

9.0 PRECISION AND ACCURACY

9.1 The precision of this method is estimated to be 20 percent at the 95 percent confidence level.

9.2 The accuracy of this method has not been established; however, repeated determinations on solutions of known concentrations do not indicate a significant bias.

10.0 REFERENCES

1. Moore, F. L., 1958. "Radiochemical Determination of Ionium in Uranium Fluorination Ash," Analytical Chemistry, 30, p. 1020.

2. Johns, F. B., P. B. Hahn, D. J. Thome and E. W. Bretthauer, Editors; March, 1979. Radiochemical Analytical Procedures for Analysis of Environmental Samples; EMSL-LV-0539-17.

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DETERMINATION OF THORIUM (ALPHA-EMITTING) ISOTOPES IN AIR FILTERS
(Method EC-264)

1.0 SCOPE AND APPLICATION

1.1 This method is applicable for determining the isotopes of thorium in paper and Hollingsworth-types filters.

1.2 At Oak Ridge National Laboratory (ORNL), the lowest reported concentration of thorium in air filters is 0.04 pCi/total filter sample when a chemically purified sample, realizing an 80 percent recovery, is counted for 1000 min on an alpha pulse-height analyzer with a detector having a 20 percent efficiency and a 0.005 cpm background over each energy region of interest.

1.3 At other plants, the lowest reported concentration is 0.4 pCi/total filter sample.

2.0 SUMMARY OF METHOD

2.1 Thorium-234 tracer (an alpha emitter) is equilibrated with the thorium isotopes in the dissolved-filter solution.

2.2 The thorium isotopes are adsorbed on an anion exchange resin, eluted with strong HCl, and coprecipitated with praseodymium as the hydroxide and fluoride.

2.3 The thorium is finally purified by extracting with thenoyltrifluoroacetone (TTA)-xylene.

2.4 The TTA extract is dried on a stainless steel disc; the chemical yield is determined by measuring the recovered ^{234}Th by beta counting.

2.5 The alpha-emitting thorium isotopes are determined by an alpha pulse-height analysis.

3.0 INTERFERENCES

3.1 This method does not separate uranium adequately when the uranium/thorium activity ratio is greater than 10. Several of the isotopes of uranium and thorium have alpha energies sufficiently close to cause interferences in pulse-height analysis. Further purification procedures are recommended when the uranium/thorium ratio is known to be greater than 10.

4.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

4.1 Filters should be handled as little as possible to avoid loss of particulates and should be stored in plastic containers, such as polyethylene bags.

5.0 APPARATUS AND EQUIPMENT

5.1 Vortex mixer.

5.2 Hot plate.

5.3 Centrifuge.

5.4 Extraction vials - 50 mL, with plastic-lined screw caps.

5.5 Transfer pipets.

5.6 Beakers - 250 mL; also a size adequate to accommodate the sample aliquot.

5.7 pH meter with combination electrode.

5.8 Stainless steel discs - sized to be compatible with counting equipment.

5.9 Multichannel analyzer system with silicon surface-barrier detector(s).

5.10 Beta counter - adequate to accommodate the stainless steel discs.

5.11 Plastic centrifuge tubes - 50 and 100 mL.

5.12 Water bath.

5.13 Teflon beakers - 250 mL.

5.14 Analytical balance.

5.15 Muffle furnace.

5.16 Glass ion-exchange column - 8-mm I.D. by 25-cm long, fitted with a stopcock and a reservoir.

6.0 REAGENTS

6.1 Praseodymium solution (5 mg/mL) - Dissolve 6.00 g of $Pr(NO_3)_3 \cdot 6H_2O$ in dilute (2 M) HNO_3 and dilute to 500 mL with water.

6.2 Ammonium hydroxide - Concentrated.

6.3 Potassium dichromate (0.4 M) - Dissolve 11.8 g of $K_2Cr_2O_7$ in water and dilute to 100 mL.

6.4 Hydrofluoric acid - Concentrated.

6.5 Aluminum nitrate solution (2 M) - Dissolve 75.0 g of $Al(NO_3)_3 \cdot 9H_2O$ in water and dilute to 100 mL.

6.6 Nitric acid - Concentrated.

6.7 Nitric acid (1 M) - Dilute 6.25 mL of concentrated HNO_3 to 100 mL with water.

6.8 Nitric acid solution (pH 1.5) - Transfer 500 mL of water to an 800-mL beaker. Immerse the pH electrode, stir, and adjust the pH to 1.5 with concentrated HNO_3.

6.9 TTA-xylene solution (0.5 M TTA) - Dissolve 55.5 g of TTA (thenoyltrifluoroacetone) in xylene and dilute to 500 mL with xylene.

6.10 Thorium tracer (^{234}Th) - Dissolve 1 g of isotopically depleted U_3O_8 in dilute nitric acid and convert to the chloride by boiling down several times with HCl, then taking the residue to dryness. Dissolve the uranium chloride in 8 M HCl and extract the uranium with 20 percent (w/v) Adogen 364 in xylene. Retain the aqueous phase for the thorium tracer. Take the solution to dryness on a hot plate and convert to the nitrate by boiling down several times with concentrated HNO_3. Take up the Th tracer in 10 mL of 8 M HNO_3 and determine the ^{234}Th beta activity.

6.11 Ammonium hydroxide (dilute) - Dilute 35 mL of concentrated NH_4OH to 500 mL with water.

6.12 Hydrofluoric acid-nitric acid solution (1 M HF - 1 M HNO_3). Mark a polyethylene bottle at the 100mL volume level. Add 75 mL of water to the bottle. Using a plastic pipet, add 4 mL of concentrated HF; add 6.25 mL of concentrated HNO_3; and dilute to the 100mL mark with water.

6.13 Hydrochloric acid - Concentrated.

6.14 Anion-exchange resin - Dowex 1-X4 (50 to 100 mesh, chloride form), or equivalent.

6.15 Hydrochloric acid (8 M) - Add 666 mL of concentrated HCl to 334 mL of water.

6.16 Adogen 364-xylene solution, 20 percent (w/v). Weigh 20 g of Adogen 364 (or equivalent) and dilute to 100 mL with xylene.

6.17 Hydrogen peroxide - 30 percent H_2O_2.

7.0 PROCEDURE

7.1 Take the whole filter or a representative aliquot of the filter(s) and place in an adequately sized beaker. Relate the weight of aliquot to the total sample weight to determine the air flow related to the aliquot.

7.2 Place the beaker and sample in a muffle furnace and set the temperature to 210°C until carbonized.

7.3 Allow the sample to remain at 210°C until carbonized.

7.4 Raise the temperature of the furnace to 375°C and allow the sample to ash at this temperature for 16 h; finally ash at 525°C for 24 h.

7.5 Transfer the ashed sample to a 250-mL Teflon beaker.

7.6 Add 25 mL of concentrated HNO_3 and 25 mL of concentrated HF. Paper filters might be completely soluble in HNO_3, in which case the addition of HF is not necessary, and the procedure can be continued at Section 7.14.

7.7 Place the sample on a hot plate and take to dryness.

7.8 Repeat Sections 7.6 and 7.7 twice.

7.9 Add 15 mL of concentrated HNO_3 and take to dryness.

7.10 Repeat Section 7.9 twice.

7.11 Take up the residue in 25 mL of 8 M HNO_3 and 3 to 5 mL of 30 percent H_2O_2.

7.12 Transfer the sample to the original ashing beaker.

7.13 Place the beaker on a hot plate and digest with the addition of 30 percent H_2O_2 in 1-mL portions until the solution is clear.

7.14 Add 5000 to 10,000 cpm of thorium-234 tracer and 5 mL of 2 M $Al(NO_3)_3$ solution.

7.15 Adjust the volume to about 50 mL and the acidity to 8 M HNO_3 by evaporation and/or the addition of concentrated HNO_3.

7.16 Prepare a resin column as follows.

7.16.1 Place a glass-wool plug in the bottom of the column described in Section 5.16.

7.16.2 Slurry the resin (see Section 6.14) with water and immediately discard the fines by decanting. Repeat as necessary until the fines are removed.

7.16.3 Transfer 4 mL of resin to the column with water. Prevent channeling any by maintaining the solution level above the resin by use of the stopcock.

7.16.4 Place a glass-wool plug on top of the resin.

7.16.5 Convert the resin to the nitrate form by passing several volumes of column 8 M HNO_3 through the column until the resin is free of chloride ions.

7.17 Transfer the sample solution, cooled to room temperature, to the prepared resin column, and allow it to flow through the column at a rate of 2 mL/min. Discard the effluent solution.

7.18 Rinse the beaker with 25 mL of 8 M HNO_3 and transfer the rinse to the column. Allow the 8 M HNO_3 rinse to flow through the column at a rate of mL per minute. Discard the effluent solution.

7.19 Place a clean 250-mL beaker under the column.

7.20 Add 25 mL of 8 M HCl to the column and adjust the flow to 2 mL/min; retain the column effluent.

7.21 Repeat Section 7.20.

7.22 Add 1 mL of praseodymium solution to the beaker containing the column effluent from Sections 7.20 and 7.21.

7.23 Place the beaker on a hot plate and reduce the volume to approximately 10 mL.

7.24 Add concentrated ammonium hydroxide slowly with stirring to a pH of 9.

7.25 Stir the sample sufficiently to induce coalescence of the precipitate and allow the precipitate to settle (preferably overnight).

7.26 Decant the supernatant solution, and quantitatively transfer the precipitate to a 50- or 100-mL centrifuge tube.

7.27 Centrifuge at 2000 rpm for about 10 min.

7.28 Discard the supernatant solution.

7.29 Wash the precipitate with water, centrifuge, and discard the water wash solution.

7.30 Dissolve the precipitate with 8 to 10 drops of concentrated nitric acid.

7.31 Add approximately 0.3 mL of 0.4 M potassium dichromate.

7.32 Digest in a hot water bath, that is at or near the boiling point, for 10 min.

7.33 Remove from the bath and add approximately 0.3 mL of concentrated hydrofluoric acid. Mix well and allow to digest at room temperature for 10 min.

7.34 Centrifuge at 2000 rpm for 5 min.

7.35 Add two drops of praseodymium solution and swirl gently without disturbing the precipitate.

7.36 Repeat Section 7.34.

7.37 Discard the supernatant solution.

7.38 Wash the precipitate with approximately 2 mL of 1 M HF - 1 M HNO_3 solution that contains three drops of 0.4 M potassium dichromate.

7.39 Repeat Sections 7.34 and 7.37.

7.40 Dissolve the fluoride precipitate with 0.5 mL of 2 M aluminum nitrate and 5 drops of 1 M HNO_3.

7.41 Transfer the solution to a 50-mL vial.

7.42 Rinse the centrifuge tube with 5 mL of distilled water and add the rinse solution to the 50-mL vial.

7.43 With the aid of the pH meter, adjust the pH of the solution to between 1.4 and 1.5 with dilute ammonium hydroxide and/or dilute nitric acid.

7.44 Add 2 mL of 0.5 M TTA-xylene.

7.45 Mix on the Vortex mixer for 10 min.

7.46 Centrifuge at 2000 rpm for about 5 min.

7.47 Transfer the upper phase (TTA-xylene) to a new vial.

7.48 Repeat Sections 7.44 through 7.47, transferring the second TTA extract to the same vial.

7.49 Scrub the TTA extract with 5 mL of pH 1.5 nitric acid solution.

7.50 Repeat Section 7.46 and discard the scrub solution.

7.51 Evaporate the entire TTA extract on a stainless steel disc, adding portions in small increments. Flame the disc to a red heat.

7.52 Take an aliquot of ^{234}Th identical with that used in Section 7.14. Evaporate it on a stainless steel disc, adding portions in small increments, to provide a comparator disc. Flame the disc to a red heat.

7.53 Count the sample disc and the ^{234}Th comparator disc on a beta counter. Divide the sample net beta count by the comparator net beta count to determine the fraction of thorium recovery.

7.54 Perform an alpha pulse-height analysis to determine the identity and quantity of the thorium isotopes present in the sample.

8.0 CALCULATIONS

Thorium isotopes on the filter sample are calculated using the following equation.

$$\text{Thorium-x (pCi)} = A/(B \cdot C \cdot D)$$

where:

x = isotope of interest

A = The net integrated count rate (cpm) of thorium-x from the pulse-height analysis

B = The efficiency factor of the alpha pulse-height analyzer system (cpm/dpm)

C = The conversion factor (2.22 dpm/pCi)

D = The fraction of ^{234}Th recovered.

Thorium isotopes in air are calculated using the following equation:

$$\text{Thorium-x } (\text{pCi/m}^3) = A/(B\cdot C\cdot D\cdot V)$$

where:

A, B, C, and D are as above

V = Volume of air (m^3) (See Section 7.1.)

9.0 PRECISION AND ACCURACY

9.1 The relative precision of this method is estimated to be 20 percent at the 95 percent confidence level.

9.2 The accuracy of this method has not been established; however, repeated determinations on solutions of known concentrations do not indicate a significant bias.

10.0 REFERENCES

1. Moore, F. L, 1958. "Radiochemical Determination of Ionium in Uranium Fluorination Ash"; Analytical Chemistry, 30, p. 1020.

DETERMINATION OF THORIUM IN WATER
(Method EC-187A)

1.0 SCOPE AND APPLICATION

1.1 This method covers the determination of trace levels of thorium in stream, lake, and drinking water samples.

1.2 The lowest reported concentration of thorium in water is 0.002 mg/L using a 2-L sample.

2.0 SUMMARY OF METHOD

2.1 The sample is digested with nitric acid and evaporated to dryness. The residue is taken up in dilute nitric acid and any insoluble material is removed by filtration.

2.2 The sample is again evaporated to dryness and placed in a dilute hydrochloric acid solution. Thorin, o-[(2-hydroxy-3,6-disulfo-1-naphthyl)azo] benzenear-sonic acid disodium salt, is added. It reacts with thorium to form a chromophore that absorbs at 545 nm.

3.0 INTERFERENCES

3.1 The greatest interference is due to Fe^{+3}. This interference may be eliminated by reduction to Fe^{+2} with hydroxylamine hydrochloride. An Alamine 336-toluene extraction may be necessary to eliminate interference from a large amount of Fe^{+3}.

3.2 Zirconium and titanium also interfere in this method.

4.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

4.1 Samples may be preserved by adjusting the pH to < 2.0 with nitric acid.

5.0 APPARATUS AND EQUIPMENT

5.1 Spectrophotometer - UV-Vis, equipped with 1-cm cells.

5.2 Separatory funnels - 125 mL.

6.0 REAGENTS

6.1 Hydrochloric acid solution (6 M) - Add 125 mL of concentrated HCl to 100 mL of deionized water and dilute to 250 mL.

6.2 Hydrofluoric acid solution (0.5 M) - Add 2 mL of concentrated HF to 50 mL of deionized water and dilute to 100 mL. Store in a plastic container.

6.3 Hydroxylamine hydrochloride solution (10 percent w/v) - Dissolve 25.0 g of hydroxylamine hydrochloride in deionized water and dilute to 250 mL.

6.4 Thorin solution (0.15 percent w/v) - Dissolve 3.00 g of thorin in 500 to 800 mL of deionized water with constant stirring. Dilute to 2000 mL with deionized water and filter to remove any insoluble material.

6.5 Thorium stock solution (1000 ug/mL) - Dissolve 1.00 g of clean thorium metal in 1:1 nitric acid to which has been added a drop of hydrofluoric acid. Dilute to 1000 mL with deionized water.

6.6 Thorium working standards. Dilute portions of the thorium stock solution to 1000 mL with deionized water according to the following schedule:

Volume of stock solution (mL)	Concentration of working standard (ug/mL)
2	2
5	5
20	20
40	40
60	60
80	80
100	100

6.7 Alamine 336-toluene solution, 10 percent v/v. Dissolve 10 mL of Alamine 336 (a technical mixture of quaternary amines) in toluene and dilute to 1000 mL with toluene.

7.0 CALIBRATION

7.1 Transfer 1.0 mL of each working standard to a 10-mL volumetric flask.

7.2 Add 0.5 mL of 6 M HCl, 1 mL of 10 percent hydroxylamine hydrochloride solution, and 1 mL of 0.15 percent thorin solution to each flask, dilute to volume with deionized water, and mix.

7.3 Determine the absorbance of each standard against a reagent blank at 545 nm and construct a calibration curve of concentration versus absorbance, or calculate a calibration factor by dividing ug thorium by absorbance.

8.0 PROCEDURE

8.1 Transfer a 1- to 2-L aliquot of the well-mixed sample to an adequately sized beaker.

8.2 Add 100 mL of concentrated HNO_3, cover with a watch glass, and evaporate slowly to near-dryness on a hot plate.

8.3 Carefully wash the watch glass and sides of the beaker with a small amount of concentrated HNO_3.

8.4 Replace the beaker on a hot plate and evaporate just to dryness. Do not bake the residue.

8.5 Remove the beaker from the hot plate, allow to cool, and dissolve the residue with a few mL of 2 M HNO_3.

8.6 Filter the sample through Whatman 41 paper to remove insolubles. Wash the filter with 2 M HNO_3.

8.7 Collect the filtrate and washings in a 50-mL volumetric flask and dilute to volume with 2 M HNO_3.

8.8 Transfer a 20-mL aliquot to a 50-mL beaker and add 4 mL of concentrated HNO_3 and a drop of 0.5 M HF.

8.9 Place the beaker on a hot plate and, without boiling, evaporate just to dryness.

8.10 Remove from the hot plate, cool, and add 0.5 mL of 1:1 HCl to dissolve the residue. Add 1 mL of 10 percent hydroxylamine hydrochloride solution and briefly warm on a hot plate.

8.11 If the solution is clear, proceed to Section 8.18. If the solution is cloudy, proceed to Section 8.12.

8.12 Place the beaker on a hot plate and evaporate just to dryness.

8.13 Dissolve the residue with a few mL of 9 M HCl and transfer to a 125-mL separatory funnel with 9 M HCl. The total volume after transfer should be 15 mL.

8.14 Add 20 mL of 10 percent Alamine 336 in toluene solution and extract for 1 min.

8.15 Drain the aqueous layer into a 50-mL beaker through a piece of 1-in. Whatman 41 paper in a small conical funnel. Wash the paper with a few mL of 9 M HCl. Discard the organic phase.

8.16 Place the beaker on a hot plate and evaporate just to dryness.

8.17 Repeat Section 8.10.

8.18 Transfer the sample solution to a 10-mL volumetric flask with deionized water.

8.19 Add 1 mL of 0.15 percent thorin solution, dilute to volume, and mix.

8.20 Measure the absorbance of the sample at 545 nm, against a reagent blank carried through the above steps.

9.0 CALCULATION

9.1 From the calibration curve, or using the calibration factor, determine the ug/mL thorium of the sample as measured.

9.2 Calculate the mg/L of thorium in the original sample using the following equation:

$$\text{mg/L} = \frac{A}{1000} \times \frac{10}{20} \times \frac{50}{B} = \frac{A}{B} \times \frac{25}{1000}$$

where:

A = Thorium from calibration curve (ug/mL)

B = Volume of sample (mL).

10.0 PRECISION AND ACCURACY

10.1 The method for determining trace levels of thorium in water has a relative standard deviation of 5 percent.

10.2 In the absence of interferences, the method has no recognized bias.

11.0 REFERENCE

1. Thomason, P. F., M. A. Perry and W. M. Byerly 1949. "Determination of Microgram Amounts of Thorium," Anal. Chem., Vol. 21, p. 1239.

DETERMINATION OF THORIUM IN SEDIMENT AND SOIL
(Method EC-360)

1.0 SCOPE AND APPLICATION

1.0 This method covers the determination of trace levels of thorium in sediment and soil samples.

1.2 The lowest reported concentration of thorium in sediment and soil is 3 ug/g using a 5-g sample.

2.0 SUMMARY OF METHOD

2.1 The sample is digested with nitric acid and the solid residue removed by filtration.

2.2 A portion of the digestate is extracted with Alamine 336 in toluene to minimize interferences.

2.3 Thorin, o-[(2-hydroxy-3,6-disulfo-1-naphthyl)azo] benzenearsonic acid disodium salt, is added. It reacts with thorium to form a chromophore that absorbs at 545 nm.

3.0 INTERFERENCES

3.1 Ferric ion interference is eliminated by the Alamine 336-toluene extraction.

4.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

4.1 The sample is dried to a constant weight at 105°C, pulverized, screened to 100 mesh, and blended.

4.2 The prepared sample may be stored in an airtight glass or plastic container.

5.0 APPARATUS AND EQUIPMENT

5.1 Spectrophotometer - UV-Vis, equipped with 1-cm cells.

5.2 Separatory funnels - 125 mL.

6.0 REAGENTS

6.1 Hydrochloric acid solution (6 M) - Add 125 mL of concentrated HCl to 100 mL of deionized water and dilute to 250 mL.

6.2 Hydrofluoric acid solution (0.5 M) - Add 2 mL of concentrated HF to 50 mL of deionized water and dilute to 100 mL. Store in a plastic container.

6.3 Hydroxylamine hydrochloride solution (10 percent w/v) - Dissolve 25 g of hydroxylamine hydrochloride in deionized water and dilute to 250 mL.

6.4 Thorin solution (0.15 percent w/v) - Dissolve 3.000 g of thorin in 500 to 800 mL of deionized water with constant stirring. Dilute to 2000 mL with deionized water and filter to remove any insoluble material.

6.5 Thorium stock solution (1000 ug/mL) - Dissolve 1.00 g of clean thorium metal in 1:1 nitric acid to which has been added a drop of hydrofluoric acid. Dilute to 1000 mL with deionized water.

6.6 Thorium working standards. Dilute portions of the thorium stock solution to 1000 mL with deionized water according to the following schedule:

Volume of stock solution (mL)	Concentration of working standard (ug/mL)
2	2
5	5
20	20
40	40
60	60
80	80
100	100

6.7 Alamine 336-toluene solution, 10 percent v/v. Dissolve 10 mL of Alamine 336 (a technical mixture of quaternary amines) in toluene and dilute to 1000 mL with toluene.

7.0 CALIBRATION

7.1 Transfer 1.0 mL of each working standard to a 10-mL volumetric flask.

7.2 Add 0.5 mL of 6 M HCl, 1 mL of 10 percent hydroxylamine hydrochloride solution, and 1 mL of 0.15 percent thorin solution to each flask; dilute to volume with deionized water, and mix.

7.3 Determine the absorbance of each standard against a reagent blank at 545 nm and construct a calibration curve of concentration versus absorbance, or calculate a calibration factor by dividing ug thorium by absorbance.

8.0 PROCEDURE

8.1 Weigh 5 g of dry sample and place in a beaker.

8.2 Add enough concentrated HNO_3 to just cover the sample, approximately 15 mL.

8.3 Heat to boiling for 10 min on a stirrer/hot plate with constant stirring.

8.4 Remove the sample from the hot plate and, after the solids have settled, decant the acid into a 400-mL beaker.

8.5 Repeat Sections 8.2 through 8.4 twice more.

8.6 Add 50 mL of deionized water to the solids, warm on the hot plate, and filter through Whatman 41 paper into the 400-mL beaker.

8.7 Rinse the residue and filter paper with liberal amounts of 4 M HNO_3. Discard the residue.

8.8 Evaporate the combined digestates and rinse to approximately 10 mL, cool, and transfer to a 50-mL volumetric flask; dilute to volume with 2 M HNO_3.

8.9 Transfer a 5-mL portion of sample to a 50-mL beaker. Add 4 mL of concentrated HNO_3 and 1 drop of 0.5 M HF.

8.10 Place the beaker on a hot plate and, without boiling, evaporate just to dryness.

8.11 Dissolve the residue with a few mL of 9 M HCl and transfer to a 125-mL separatory funnel with 9 M HCl. The total volume after transfer should be 15 mL.

8.12 Add 20 mL of 10 percent Alamine 336 in toluene solution and extract for 1 min.

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8.13 Drain the aqueous layer into a 50-mL beaker through a piece of 1-in. Whatman 41 paper in a small conical funnel. Wash the paper with a few mL of 9 M HCl. Discard the organic layer.

8.14 Place the beaker on a hot plate and evaporate to dryness.

8.15 Remove from the hot plate, cool, and add 0.5 mL of 1:1 HCl to dissolve the residue. Add 1 mL of 10 percent hydroxylamine hydrochloride solution and briefly warm on a hot plate.

8.16 Transfer the sample solution to a 10-mL volumetric flask with deionized water.

8.17 Add 1 mL of 0.15 percent thorin solution, dilute to volume, and mix.

8.18 Measure the absorbance of the sample at 545 nm against a reagent blank carried through the above steps.

9.0 CALCULATION

9.1 From the calibration curve, or using the calibration factor, determine the ug/mL thorium of the sample as measured.

9.2 Calculate the ug/g thorium in the original sample using the following equation:

$$\text{ug/g} = A \times \frac{10}{5} \times \frac{50}{B} = \frac{A}{B} \times 100$$

where:

A = Thorium from calibration curve (ug/mL)

B = Weight of sample in grams.

10.0 PRECISION AND ACCURACY

10.1 This method has a relative standard deviation of 5 percent.

10.2 With the removal of interferences, some thorium may be lost, contributing to a small negative bias, not yet defined.

11.0 REFERENCE

1. Thomason, P. F., M. A. Perry, and W. M. Byerly, 1949. "Determination of Microgram Amounts of Thorium" Anal. Chem., Vol. 21, p. 1239.

DETERMINATION OF STRONTIUM-90 IN WATER
(Method EC-184)

1.0 SCOPE AND APPLICATION

1.1 This method is applicable for determining the presence of ^{90}Sr in potable, natural, and industrial waters.

1.2 At Oak Ridge National Laboratory (ORNL), the lowest reported concentration of ^{90}Sr in water is 0.004 pCi/mL when analyzing a 1-L sample, counting for 30 min on a beta counter with a 0.6-cpm background and a 25 percent efficiency, and realizing an 80 percent chemical recovery of the strontium carrier.

1.3 At other plants, the lowest reported concentration of ^{90}Sr in water is 0.02 pCi/mL for a 1-L sample aliquot.

2.0 SUMMARY OF METHOD

2.1 Strontium carrier is equilibrated with the sample, precipitated as the insoluble carbonate, and separated from calcium and magnesium by nitrate precipitations followed by acetone washes. Further purification is accomplished by removing impurities with hydroxide scavenging and by removing barium as the chromate; final purification is made by precipitation of strontium as the oxalate which is mounted for beta counting and counted on a low-background beta counter.

3.0 INTERFERENCES

3.1 Strontium-89, when present in the sample, interferes with the beta counting of strontium-90. The presence of ^{89}Sr can be ascertained by absorption studies; the interference of ^{89}Sr can be circumvented by indirect determination of ^{90}Sr via the ^{90}Y daughter, after adequate ingrowth.

3.2 Strontium-90 is self-absorbing; therefore, the counting efficiency must be corrected for the amount of solids on the mounts.

4.0 SAMPLE HANDLING AND PRESERVATION

4.1 Samples are adjusted to a pH of 1.0 with nitric acid as soon as practicable, unless suspended and/or soluble strontium determinations are separately needed, in which case the samples are filtered before being adjusted with acid.

4.2 After preliminary treatment, the samples are stored in either glass or plastic containers.

5.0 APPARATUS AND EQUIPMENT

5.1 Laboratory glassware.

5.2 Beakers - Size adequate for sample aliquot.

5.3 Centrifuge tubes - 50-mL glass.

5.4 Centrifuge.

5.5 Hot plate.

5.6 Ice bath.

5.7 Filter paper - No. 541 Whatman (11-cm).

5.8 Filter paper - No. 1 Whatman (18-mm).

5.9 Analytical balance.

5.10 Filter flask and funnel.

5.11 Fritted-glass filter crucibles.

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5.12 Desiccator.

5.13 Low-background beta counter.

5.14 Hot plate with magnetic stirrer.

5.15 Magnetic stirring bar - Teflon-coated, 1.5-in. long.

6.0 REAGENTS

6.1 Acetic acid (6 M) - Add 340 mL of glacial acetic acid (CH_3COOH) to 500 mL of water and dilute to 1 L with water.

6.2 Ammonium acetate solution (6 M) - Dissolve 462 g of ammonium acetate ($NH_4C_2H_3O_2$) in 500 mL of water and dilute to 1 L with water.

6.3 Sodium carbonate solution (2 M) - Dissolve 248 g of sodium carbonate monohydrate ($Na_2CO_3 \cdot H_2O$) in 700 mL of water and dilute to 1 L with water.

6.4 Ammonium oxalate solution (saturated) - Add 200 g of ammonium oxalate monohydrate [$(NH_4)_2C_2O_4 \cdot H_2O$] to 500 mL of water in a 1-L container, dilute to 1 L with water, mix thoroughly, and let stand overnight before using.

6.5 Sodium chromate solution (1.5 M) - Dissolve 176 g of sodium chromate quadrihydrate ($Na_2CrO_4 \cdot 4H_4O$) in water and dilute to 500 mL with water.

6.6 Barium carrier solution (10 mg Ba/mL) - Dissolve 19.0 g of barium nitrate [$Ba(NO_3)_2$] in water and dilute to 1 L with water.

6.7 Nitric acid - Fuming.

6.8 Ferric nitrate solution (50 percent) - Dissolve 100 g of ferric nitrate nonahydrate [$Fe(NO_3)_3 \cdot 9H_2O)$] in water and dilute to 100 mL with water.

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6.9 Ferric nitrate solution (0.1 M) - Dissolve 40.4 g of ferric nitrate nonahydrate [$Fe(NO_3)_3 \cdot 9H_2O$] in water and dilute to 1 L with water.

6.10 Nitric acid (6 M) - Add 375 mL of concentrated HNO_3 to 500 mL of water and dilute to 1 L with water.

6.11 Acetone.

6.12 Sodium hydroxide solution (19 M) - Add 760 g of sodium hydroxide (NaOH) slowly with stirring to 500 mL of water and dilute to 1 L with water. Store in a plastic container.

6.13 Ethyl alcohol - 95 percent C_2H_5OH.

6.14 Diethyl ether - Anhydrous $C_2H_5OC_2H_5$.

6.15 Ammonium hydroxide - Concentrated.

6.16 Strontium carrier solution - Dissolve 27.3 g of strontium nitrate [$Sr(NO_3)_2$] in a minimum of nitric acid and dilute to 1 L with water.

6.16.1 Standardization of strontium carrier - Pipet 5.00 mL of strontium carrier solution into a 100-mL beaker and add 30 mL of water. Adjust the pH to 9.0 with concentrated NH_4OH, add 10 mL of saturated $(NH_4)_2C_2O_4$ solution, and heat to nearly boiling with stirring. Cool to room temperature and quantitatively transfer the precipitate to a previously tared filter crucible with hot water. Wash the precipitate several times with hot water, three times with 10-mL portions of ethyl alcohol, and two times with 10-mL portions of diethyl ether. Desiccate the crucible and precipitate under vacuum to a constant weight. The net weight of the precipitate is the weight of strontium oxalate monohydrate ($SrC_2O_4 \cdot H_2O$) in 5.00 mL of the strontium carrier solution.

6.17 Phenolphthalein indicator solution (5 percent w/v) - Dissolve 5 g of phenolphthalein ($C_{20}H_{14}O_4$) in 50 mL of 95 percent ethyl alcohol and dilute to 100 mL with water.

6.18 Nitric acid - Concentrated.

7.0 PROCEDURE

7.1 Transfer a measured volume of the sample to an adequately sized beaker and adjust to a pH of 1.0 with nitric acid.

7.2 Add 1.00 mL of the standardized strontium carrier solution and 1 mL of 50 percent ferric nitrate solution.

7.3 Place on a hot plate and heat with stirring to near boiling. Digest for 20 min.

7.4 Cautiously add 19 M NaOH with stirring to a pH of 10.

7.5 Add 50 mL of 2 M Na_2CO_3 solution and continue to digest on the hot plate with stirring for 30 min.

7.6 Remove from the hot plate and allow the precipitate to settle overnight.

7.7 Decant the supernatant liquid and discard it.

7.8 Transfer the precipitate to a 50-mL glass centrifuge tube, centrifuge for 5 min at 1500 rpm, and discard the supernatant liquid.

7.9 Wash the precipitate with 30 mL of water, centrifuge, and discard the wash solution.

7.10 Dissolve the precipitate in a minimum of concentrated HNO_3, then add 25 mL of fuming nitric acid.

7.11 Place the tube in an ice bath and stir the solution until precipitation is complete.

7.12 Remove the tube from the ice bath and centrifuge at 1500 rpm for 5 min. Decant the supernatant solution into a large volume of water and discard. Drain the tube completely, leaving no trace of HNO_3, as a precaution against any adverse reaction with the acetone wash that follows.

7.13 Add 30 mL of acetone and wash the precipitate thoroughly with stirring.

7.14 Centrifuge for 5 min at 1500 rpm and decant the acetone wash solution into a clearly marked organic waste container.

7.15 Dissolve the precipitate in a minimum of water.

7.16 Repeat Sections 7.10 through 7.14 starting with the addition of fuming HNO_3 in Section 7.10.

7.17 Dissolve the precipitate in 10 mL of water.

7.18 Add two drops of phenolphthalein indicator solution and 0.5 mL of 0.1 M $Fe(NO_3)_3$ solution.

7.19 Add concentrated NH_4OH dropwise with stirring until the phenophthalein end point is reached, then add 5 more drops.

7.20 Centrifuge for 5 min at 1500 rpm.

7.21 Filter the supernatant solution through No. 541 filter paper into another 50-mL glass centrifuge tube. Wash the filter with 3 mL of water and discard the precipitate. Record the time at which the filtering is done as the separation time of ^{90}Sr from ^{90}Y.

7.22 Neutralize the solution with 6 M HNO_3; then add 1 mL of 6 M acetic acid, 2 mL of 6 M ammonium acetate, and 1 mL of barium carrier.

7.23 Heat the solution to near boiling; add 1.5 M Na_2CrO_4 solution dropwise with stirring to precipitate barium chromate. Chill in an ice bath and stir to complete the precipitation. Check for complete precipitation of barium by adding a few more drops of Na_2CrO_4.

7.24 Centrifuge for 5 min at 1500 rpm.

7.25 Filter the supernatant solution through No. 541 filter paper into another 50-mL glass centrifuge tube and wash the filter with 3 mL of water. Discard the precipitate.

7.26 Add 2 mL of concentrated NH_4OH to the solution and heat to boiling.

7.27 Add 5 mL of saturated ammonium oxalate solution with stirring to precipitate the strontium oxalate.

7.28 Chill in an ice bath and continue to stir to complete the precipitation.

7.29 Centrifuge for 5 min at 1500 rpm and discard the supernatant solution.

7.30 Place a tared 18-mm No. 1 Whatman filter paper in the filtering funnel and wet with water, using vacuum on the filtering flask.

7.31 Transfer the precipitate onto the filter with hot water; then wash with two 10-mL portions of hot water, three 5-mL portions of 95 percent ethyl alcohol, and two 5-mL portions of diethyl ether.

7.32 Weigh the filter paper and precipitate, determine the chemical recovery, and mount for beta counting.

7.33 Count the sample mount without delay on a low-background beta counter.

8.0 CALCULATIONS

Strontium-90 in water is calculated using the following equation.

$$^{90}\mathrm{Sr},\ \mathrm{pCi/mL} = A \cdot B \cdot C / D \cdot V$$

where:

A = Net counts per minute of purified ^{90}Sr (no ^{89}Sr interference)

B = Efficiency factor for ^{90}Sr, including self-absorption correction

C = Conversion factor from dpm to pCi = 1 pCi/2.22 dpm

D = Fraction of strontium carrier recovered

V = Volume of sample (mL).

9.0 PRECISION AND ACCURACY

9.1 The precision of this method at the 95 percent confidence level is ±12 percent.

9.2 The method exhibits a negative bias of 5 percent when applied to controls of known ^{90}Sr concentration.

10.0 REFERENCES

1. Hanh, R. B. and C. P. Straub, 1955. "Determination of Radioactive Strontium and Barium in Water," J. Am. Water Works Assoc., 47, No. 4, 335.

2. Kooi, J., 1958. "Quantitative Determination of Strontium-89 and Strontium-90 in Water," Anal. Chem., 30, p. 532.

3. Franson, M. A., Editor, 1975. Standard Methods for Examination of Water and Waste Water, 14th Edition.

DETERMINATION OF STRONTIUM-90 IN SEDIMENT AND SOIL
(Method EC-350)

1.0 SCOPE AND APPLICATION

1.1 This method is applicable for determining the presence of strontium-90 in soil and sediment samples.

1.2 At Oak Ridge National Laboratory (ORNL), the lowest reported concentration of ^{90}Sr in sediment and soil is 0.2 pCi/g when analyzing a 10-g sample, counting for 30 min on a beta counter with a 0.6-cpm background and a 25 percent counting efficiency, and realizing an 80 percent chemical recovery for the strontium carrier.

1.3 At other plants, the lowest reported concentration is 1 pCi/g for 10-g samples.

[illegible]0 SUMMARY OF METHOD

2.1 A known weight of strontium carrier is added to the sample which is leached by hot nitric acid and hot nitric acid-hydrogen peroxide treatment. The leachate is reduced in volume, and the strontium is separated from calcium, magnesium, and rare earths by nitrate precipitation followed by acetone washes. Further purification is accomplished by removing yttrium and other impurities with hydroxide scavenging and by removing barium and radium as the chromates; final purification is made by precipitation of strontium as the oxalate, which is mounted for beta counting and counted on a low-background beta counter.

3.0 INTERFERENCES

3.1 Samples which are of a refractory nature, such as test-site materials, are not apt to release strontium in the leaching process; therefore, more rigorous treatment is recommended for decomposition of these samples.

3.2 Strontium-89, when present in the sample, interferes with the beta counting of strontium-90. The presence of ^{89}Sr can be ascertained by absorption studies; the interference of ^{89}Sr can be circumvented by indirect determination of ^{90}Sr via the ^{90}Y daughter, after adequate ingrowth.

3.3 Strontium-90 is self-absorbing; therefore, the counting efficiency varies with the amount of solids on the mounts.

4.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

4.1 The samples are oven-dried to a constant weight at 105°C, pulverized, screened to 100-mesh particle size, and thoroughly blended.

4.2 The prepared sample material is stored in airtight glass or plastic containers.

5.0 APPARATUS AND EQUIPMENT

5.1 Drying oven - 105°C.

5.2 Muffle furnace - 500°C.

5.3 Hot plate with magnetic stirrer.

5.4 Centrifuge.

5.5 Screens - 40- and 100-mesh.

5.6 Analytical balance.

5.7 Pulverizer.

5.8 Magnetic stirring bar - Teflon-coated, 1.5-in. long.

5.9 Laboratory glassware

5.9.1 Beakers - 250mL size and 500-mL tall-form.

5.9.2 Centrifuge tubes - 50-mL glass and 100-mL plastic.

5.9.3 Fritted-glass filter crucibles.

5.9.4 Filter flask and funnel.

5.10 Filter paper - 541 Whatman (11 cm).

5.11 Filter paper - 1 Whatman (18 mm).

5.12 Ice bath.

5.13 Desiccator.

5.14 Low-background beta counter.

6.0 REAGENTS

6.1 Nitric acid - Fuming.

6.2 Nitric acid - Concentrated.

6.3 Nitric acid (8 M) - Add 500 mL of concentrated HNO_3 to 500 mL of water.

6.4 Nitric acid (6 M) - Add 375 mL of concentrated HNO_3 to 500 mL of water and dilute to 1 L with water.

6.5 Ammonium hydroxide - Concentrated.

6.6 Acetic acid (6 M) - Add 340 mL of glacial acetic acid (CH_3COOH) to 500 mL of water and dilute to 1 L with water.

6.7 Ammonium acetate solution (6 M) - Dissolve 462 g of ammonium acetate ($NH_4C_2H_3O_2$) in 500 mL of water and dilute to 1 L with water.

6.8 Ammonium oxalate solution (saturated) - Add 200 g of ammonium oxalate monohydrate [$(NH_4)_2C_2O_4 \cdot H_2O$] to 500 mL of water in a 1-L container, dilute to 1 L with water, mix thoroughly, and let stand overnight before using.

6.9 Sodium chromate solution (1.5 M) - Dissolve 176 g of sodium chromate quadrihydrate ($Na_2CrO_4 \cdot 4H_2O$) in water and dilute to 500 mL with water.

6.10 Barium carrier solution (10 mg Ba/mL) - Dissolve 19.0 g of barium nitrate [$Ba(NO_3)_2$] in water and dilute to 1 L with water.

6.11 Acetone.

6.12 Hydrogen peroxide - 30 percent solution.

6.13 Phenolphthalein indicator solution (5 percent w/v) - Dissolve 5 g of phenolphthalein ($C_{20}H_{14}O_4$) in 50 mL of 95 percent ethyl alcohol and dilute to 100 mL with water.

6.14 Ethyl alcohol - 95 percent C_2H_5OH.

6.15 Diethyl ether - Anhydrous $C_2H_5OC_2H_5$.

6.16 Strontium carrier solution - Dissolve 27.3 g of strontium nitrate [$Sr(NO_3)_2$] in a minimum of nitric acid and dilute to 1 L with water.

6.16.1 Standardization of strontium carrier - Pipet 5.00 mL of strontium carrier solution into a 100-mL beaker and add 30 mL of water. Adjust the pH to 9.0 with concentrated NH_4OH, add 10 mL of saturated $(NH_4)_2C_2O_4$ solution, and heat to nearly boiling with stirring. Cool to

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room temperature and quantitatively transfer the precipitate to a previously tared filter crucible with hot water. Wash the precipitate several times with hot water, three times with 10-mL portions of ethyl alcohol, and two times with 10-mL portions of diethyl ether. Desiccate the crucible and precipitate under vacuum to a constant weight. The net weight of the precipitate is the weight of strontium oxalate monohydrate ($SrC_2O_4 \cdot H_2O$) in 5.00 mL of the strontium carrier solution.

6.17 Ferric nitrate solution (0.1 M) - Dissolve 40.4 g of ferric nitrate nonahydrate [$Fe(NO_3)_3 \cdot 9H_2O$] in water and dilute to 1 L with water.

7.0 PROCEDURE

7.1 Transfer a measured weight (5 to 10 g) of 100-mesh sample to a 500-mL tall-form beaker. If the sample is thought to contain organic matter, ash in a muffle furnace at 500°C for several hours before continuing.

7.2 Slowly add 50 to 75 mL of 8 M HNO_3 allowing sufficient time for any foaming to subside.

7.3 Add 1 mL of strontium carrier solution.

7.4 Carefully introduce a magnetic stirring bar, place on a hot plate, and digest with stirring at 90° to 95°C for one hour.

7.5 Remove from the hot plate and transfer the sample solution to a 100-mL plastic centrifuge tube.

7.6 Centrifuge for 10 min at 1500 rpm.

7.7 Decant the supernatant liquid into a 250-mL beaker and retain.

7.8 Rinse the residue from the centrifuge tube into the original 500-mL beaker with 50 to 75 mL of 8 M HNO_3.

7.9 Return to the hot plate and digest with stirring at 90° to 95°C or 1 h with the addition of a few drops of 30 percent hydrogen peroxide intermittently for a total of 5 to 10 mL.

7.10 Repeat Sections 7.5 through 7.7.

7.11 Repeat Section 7.8 using 25 mL of 1 M HNO_3.

7.12 Repeat Sections 7.9 and 7.10 and discard the residue.

7.13 Place the 250-mL beaker containing the leach solution on a hot plate and reduce the volume to 15 mL.

7.14 Transfer the sample solution to a 50-mL glass centrifuge tube, rinsing the 250-mL beaker with a minimum of fuming HNO_3.

7.15 Add fuming HNO_3 to give a total volume of 40 mL.

7.16 Place the 50-mL tube in an ice bath and digest the sample with frequent stirring for 30 min to precipitate the nitrates.

7.17 Remove the tube from ice bath and centrifuge for 10 min at 1500 rpm. Decant the supernatant solution into a large volume of water and discard.

7.18 Dissolve the precipitate in a minimum of water.

7.19 Add 15 mL of fuming HNO_3 and 15 mL of concentrated HNO_3.

7.20 Repeat Sections 7.16 and 7.17.

7.21 Drain the tube completely, leaving no trace of HNO_3, as a precaution against any adverse reaction with the acetone wash which follows.

7.22 Add 30 mL of acetone and wash the precipitate thoroughly with stirring.

7.23 Centrifuge for 5 min at 1500 rpm and decant the acetone wash into a clearly marked organic waste container.

7.24 Repeat Sections 7.18, 7.19, 7.16, and 7.17.

7.25 Repeat Sections 7.21, 7.22, and 7.23.

7.26 Dissolve the precipitate in 10 mL of water.

7.27 Add two drops of phenolphthalein indicator solution and 0.5 mL of 0.1 M $Fe(NO_3)_3$ solution.

7.28 Add concentrated NH_4OH dropwise with stirring until the phenolphthalein end-point is reached, then add 5 more drops.

7.29 Centrifuge for 5 min at 1500 rpm.

7.30 Filter the supernatant solution through No. 541 filter paper into another 50-mL glass centrifuge tube. Wash the filter with 3 mL of water and discard the precipitate. Record the time at which the filtering is done as the separation time of ^{90}Sr from ^{90}Y.

7.31 Neutralize the solution with 6 M ammonium acetate, and add 1 mL of barium carrier.

7.32 Heat the solution to near boiling; then add 1.5 M Na_2CrO_4 solution dropwise with stirring to precipitate barium chromate. Chill in an ice bath and stir to complete the precipitation. Check for complete precipitation of barium by adding a few more drops of Na_2CrO_4.

7.33 Centrifuge for 5 min at 1500 rpm.

7.34 Filter the supernatant solution through No. 541 filter paper into another 50-ml glass centrifuge tube and wash the filter with 3 mL of water. Discard the precipitate.

7.35 Add 2 mL of concentrated NH_4OH_4 to the solution and heat to boiling.

7.36 Add 5 mL of saturated ammonium oxalate solution with stirring to precipitate the strontium oxalate.

7.37 Chill in an ice bath and continue to stir to complete the precipitation.

7.38 Centrifuge for 5 min at 1500 rpm and discard the supernatant solution.

7.39 Place a tared 18-mm No. 1 Whatman filter paper in the filtering funnel and wet with water, using vacuum on the filtering flask.

7.40 Transfer the precipitate onto the filter with hot water; then wash with two 10-mL portions of hot water; three 5-mL portions of 95 percent ethyl alcohol; and two 5-mL portions of diethyl ether.

7.41 Weigh the filter paper and precipitate, determine the chemical recovery, and mount for beta counting.

7.42 Count the sample mount without delay on a low-background beta counter.

8.0 CALCULATIONS

8.1 Strontium-90 in soil and sediment will be calculated using the following equation

$$^{90}\text{Sr (pCi/mL)} = \cdot A \cdot B\ C/D \cdot V$$

where:

A = Net counts per minute of purified ^{90}Sr (no ^{89}Sr interference)

B = Efficiency factor for ^{90}Sr, including self-absorption correction

C = Conversion factor from dpm to pCi = 1 pCi/2.22 dpm

D = Fraction of strontium carrier recovered

V = Volume of sample (mL)

9.0 PRECISION AND ACCURACY

9.1 The precision of this method at the 95 percent confidence level is ±12 percent.

9.2 The method exhibits a positive bias of 25 percent when applied to controls of known ^{90}Sr concentration.

10.0 REFERENCES

1. Hanh, R. B. and C. P. Straub, 1955. "Determination of Radioactive Strontium and Barium in Water," J. Am. Water Works Assoc., 47, No. 4, 335..

2. Kooi, J., 1958. "Quantitative Determination of Strontium-89 and Strontium-90 in Water," Anal. Chem., 30, p. 532.

3. Franson, M. A., Editor, 1975. *Standard Methods for Examination of Water and Waste Water*, 14th Edition.

DETERMINATION OF IODINE-131 IN AIR FILTERS
(Method EC-242)

1.0 SCOPE AND APPLICATION

1.1 This method is applicable for determining the presence of ^{131}I adsorbed on air filters, such as activated charcoal and silver zeolites.

1.2 The lowest activity reported for a total sample when counted for 1 h on a detector with a 20 percent efficiency [relative to a 3 x 3-in. NaI(Tl) detector] and a 0.2-cpm background over the energy region of concern is 2.5 pCi.

2.0 SUMMARY OF METHOD

2.1 The sample is contained within a geometry with a known counting efficiency, and is counted for a period of time sufficient to produce the desired sensitivity on a Ge(Li) detector and pulse-height analyzer system.

2.2 The spectral data from the 364.5 keV energy region is processed by any of several accepted gamma-ray data reduction methods to determine the ^{131}I activity in the total sample.

3.0 INTERFERENCE

3.1 The high resolution afforded by the Ge(Li) spectrometry system eliminates interferences by ^{222}Rn daughters, ^{75}Se and other airborne radionuclides likely to be adsorbed on the sample material.

4.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

4.1 No special treatment is required; however, the samples should be counted as soon as possible to minimize radioactive decay losses ($T_{1/2}$ = 8.04 d).

5.0 APPARATUS AND EQUIPMENT

5.1 Polypropylene Petri dishes - 7 cm diameter x 1.8 cm height.

5.2 Beakers - 250 mL.

5.3 Teflon-coated stirring bars.

5.4 Filter funnel.

5.5 Vacuum filter flask.

5.6 Ge(Li) detector(s).

5.7 Multichannel pulse-height analyzer.

5.8 Magnetic stirrer.

6.0 REAGENTS

6.1 Ion exchange resin - Dowex 1-X8 (50 to 100 mesh), or equivalent.

6.2 Standardized ^{131}I solution. Suitable standards are available on a nonperiodic basis from NBS and several commercial suppliers.

7.0 PROCEDURE

7.1 Standardization

7.1.1 Prepare an ^{131}I standard in a Petri dish.

7.1.1.1 Transfer 23 mL of resin (Section 6.1) to a 250 mL beaker, and add enough H_2O to bring the total volume to approximately 150 mL. Add the Teflon stirring bar.

7.1.1.2 Place the beaker on the magnetic stirrer, and adjust the stirring speed so as to suspend the resin.

7.1.1.3 Add a known amount of ^{131}I standard activity in the 5000 pCi range, and continue stirring for 1 hour.

7.1.1.4 Quantitatively transfer the resin to a filter funnel, rinse with H_2O, and allow the resin to dry.

7.1.1.5 Quantitatively transfer the resin to a Petri dish, cap the dish, and seal the dish with plastic electrical tape.

7.1.2 Measure the ^{131}I in the Petri-dish standard.

7.1.2.1 Place the Petri dish on the Ge(Li) detector that is covered with a plastic bag for protection against contamination. Make sure that the resin is level.

7.1.2.2 Count until at least 10,000 net counts have accumulated in the 364.5 keV photopeak of ^{131}I; determine the net counts.

7.1.3 Compute the counting efficiency, E.

$$E\ (\text{cps/dps}) = \frac{C_s}{A \cdot t}$$

where:

C_s = Net counts of ^{131}I standard

A = ^{131}I activity of standard at count time (dps)

t = Count time (s).

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7.2 Measurement

7.2.1 Transfer the sample to a Petri dish, unless it is already contained in one. (Counting geometry will match that of the standard.)

7.2.2 Place the Petri dish on the Ge(Li) detector.

7.2.3 Count for a period sufficient to acquire the desired sensitivity.

7.2.4 Determine the net counts in the 364.5 keV energy region.

7.2.5 Subtract the relative counts measured on a blank sample from the sample counts.

8.0 CALCULATIONS

8.1 Iodine-131 in air filters will be calculated using the following equation.

$$\text{Total } {}^{131}\text{I at count time, pCi} = \frac{C_n \cdot F}{E \cdot t}$$

where:

C_n = Net counts of sample

E = Counting efficiency (cps/dps)

t = Sample counting time (seconds)

F = Conversion factor (27 pCi/dps).

PRECISION AND ACCURACY

9.1 The precision of this method at the 95 percent confidence level is ± 10 percent.

9.2 The method does not exhibit any bias.

10.0 REFERENCES

1. A Handbook of Radioactivity Measurements Procedures, NCRP Report No. 58, November 1978.

2. Radiochemical Analytical Procedures for Analysis of Environmental Samples, EMSL-LV-0539-17, March 1979.

DETERMINATION OF TECHNETIUM-99 IN WATER
(Method EC-186)

1.0 SCOPE AND APPLICATION

1.1 This method is applicable for the measurement of technetium-99 (Tc-99) in effluent and environmental water.

1.2 The lowest concentration reported is 0.3 pCi/ml, based on a 1-L sample.

2.0 SUMMARY OF METHOD

2.1 The sample is acidified with nitric acid, and potassium persulfate is added to ensure oxidation of technetium to Tc(VII). Iron(III) is added as a coprecipitant for uranium, thorium, and protactinium, and the solution is made basic. The solution is centrifuged and the Tc-99 in the supernate is counted on a beta liquid-scintillation spectrometer.

3.0 INTERFERENCES

3.1 This method is designed for samples which may contain uranium and its daughters. Radionuclides such as K-40, Sr-90, and Cs-137, which are not coprecipitated with ferric hydroxide, interfere. Interference by beta emitters with maximum energies greater than that of Tc-99 (0.3 MeV), e.g., K-40 and Cs-137, is minimized by energy-channel selection on the spectrometer.

4.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

4.1 Samples may be collected in glass or plastic containers.

4.2 Samples may be preserved by acidifying with 2 mL/L of 16 M nitric acid.

5.0 APPARATUS AND EQUIPMENT

5.1 Three-channel beta liquid-scintillation spectrometer and liquid-scintillation bottles.

5.2 Centrifuge and 50-mL plastic centrifuge tubes.

6.0 REAGENTS

6.1 Liquid-scintillation mix - Insta Gel, Packard Instrument Co.

6.2 Standard Tc-99 solution - 300,000 disintegrations/min/mL (dpm/mL).

6.3 Sodium hydroxide solution (40 percent w/v) - Dissolve 40 g of NaOH in 100 mL of H_2O.

6.4 Potassium persulfate solution (5 percent w/v) - Dissolve 5 g of $K_2S_2O_2$ in 100 mL of H_2O.

6.5 Ferric nitrate solution (10 percent w/v) - Dissolve 10 g of $Fe(NO_3)_3$, in 100 ml of H_2O.

7.0 PROCEDURE

7.1 Transfer 1 L of sample to a 1500-mL beaker.

7.2 Add 2 mL of 16 M nitric acid (HNO_3) and evaporate to between 50 and 70 mL.

7.3 Transfer the solution to a 100-mL volumetric flask and dilute to volume with water.

7.4 Pipet 20 mL from the volumetric flask into a 50-mL plastic centrifuge tube that has previously been calibrated for 40 mL.

7.5 Add 1 mL of 16 M HNO_3 and 2 mL of potassium persulfate solution, and warm in a hot water bath at approximately 70°C for 10 min. Note: $K_2S_2O_8$ oxidizes Tc to Tc(VII), which remains in solution after the $Fe(OH)_3$ precipitation (Section 7.6); Tc(IV) will coprecipitate with $Fe(OH)_3$.

7.6 Cool the sample to room temperature, add 1 mL of ferric nitrate solution, and make basic with NaOH. Ferric hydroxide percipitates. Check basicity with pH paper to ensure a $pH > 7$.

7.7 Dilute to 40 mL with water, stir well, and centrifuge for 2 min.

7.8 Pipet 2 mL of the supernate into a liquid-scintillation bottle.

7.9 Add 15 mL of the liquid-scintillation mix and shake.

7.10 Place the sample in the beta liquid-scintillation spectrometer, and allow to cool for 20 min.

7.11 Count the sample for 20 min using an energy channel of 0.05 to 0.3 MeV.

7.12 Add 50 mL of standard Tc-99 solution and count for 1 min.

7.13 Run a reagent blank for background.

8.0 CALCULATION

8.1 Technetium-99 concentrations in water are calculated using the following equation.

$$A = BC/22.2(D-C)$$

where:

A = Tc-99 in sample (pCi/mL)

B = Tc-99 in standard addition (dpm)

C = Counts/minute (cpm) of sample aliquot, corrected for background

D = c/m of sample aliquot plus standard addition, corrected for background

$$22.2 = 2.22\ (\text{d/m/pCi}) \times \frac{1000\ (\text{total mL sample})}{100\ (\text{aliq. factor})}.$$

9.0 PRECISION AND ACCURACY

9.1 The limit of error at the 95 percent confidence level is ±30 pCi/mL at 300 pCi/mL. There is no significant bias.

10.0 REFERENCE

1. Anders, Edward, November 1960. *The Radiochemistry of Technetium*, National Academy of Sciences (NAS-NS-3021).

DETERMINATION OF TECHNETIUM-99 IN SEDIMENT AND SOIL
(Method EC-365)

1.0 SCOPE AND APPLICATION

1.1 This method is applicable for measuring technetium-99 in soil and in sediment from streams, lakes, and holding-ponds.

1.2 The lowest reported concentration of technetium is 20 pCi/g for a 0.2-g aliquot of a 40-g sample.

2.0 SUMMARY OF METHOD

2.1 Technetium-99 is leached from the sample with hot nitric acid, and the solution is filtered.

2.2 Persulfate is added to ensure oxidation of Tc to +7, and iron is added as a coprecipitant of impurities; e.g., uranium and its daughters.

2.3 The solution is made basic and centrifuged. A portion of the supernate is mixed with a liquid scintillator and the ^{99}Tc is counted on a liquid-scintillation beta spectrometer.

A known amount of ^{99}Tc is added, the mixture is counted again to determine counting efficiency, and the activity of ^{99}Tc is calculated.

3.0 INTERFERENCES

3.1 Interferences include beta-emitting nuclides that are soluble in a basic solution, such as ^{90}Sr. Interference by high-energy beta emitters, such as ^{40}K, is minimized by appropriate energy-window selection on the spectrometer.

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4.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

4.1 Samples may be collected and stored in plastic or glass containers.

4.2 Samples are not dried, but are analyzed as-received. (If samples are heated in a drying oven, there is a possibility that Tc may be volatilized.)

5.0 APPARATUS AND EQUIPMENT

5.1 Liquid-scintillation beta spectrometer.

5.2 Liquid-scintillation counting vials - Plastic or glass, 20 mL.

5.3 Centrifuge for 50-mL tubes.

5.4 Centrifuge tubes - Plastic, 50 mL, scribed at the 40 mL level.

5.5 Filter paper - Whatman No. 41, size not critical.

5.6 Pipets - 50 uL.

6.0 REAGENTS

6.1 Liquid-scintillation mix - Insta Gel, Packard Instrument Co.

6.2 Potassium persulfate solution (5 percent w/v) - Dissolve 50 g of $K_2S_2O_8$ in water and dilute to 1 L.

6.3 8 M HNO_3 - Dilute 500 mL of concentrated HNO_3 to 1 L.

6.4 Ferric nitrate solution (10 percent w/v) - Dissolve 100 g of $2Fe(NO_3)_3 \cdot 9H_2O$ in water and dilute to 1 L.

6.5 Technetium-99 standard solution - 200,000 dpm/mL, prepared by appropriate dilution of standard solution from Amersham/Searle.

6.6 Sodium hydroxide solution (saturated) - Dissolve 347 g in 100 mL of H_2O.

7.0 PROCEDURE

7.1 Weigh 40 g of sample, as received, in a plastic petri dish and transfer to a 400-mL glass beaker.

7.2 Add, in increments of 5 mL, 200 mL of 8 M HNO_3. If frothing occurs with the addition of acid, add approximately 100 mL of H_2O before the addition of more acid.

7.3 Heat to between 60 to 80°C for 2 h. (Do not boil or allow to go to dryness.)

7.4 Allow solids to settle, and decant the solution into a 1 L glass beaker.

7.5 Repeat Sections 7.2, 7.3, and 7.4 two times.

7.6 Evaporate the leaching solution to 50 mL. (Do not boil or allow to go to dryness since Tc may be volatilized.)

7.7 Dilute the solution to approximately 150 mL, filter it into a 200-mL volumetric flask, and dilute to volume with 4 M HNO_3.

7.8 Pipet 20 mL of the prepared solution into a 50-mL plastic centrifuge tube scribed for 40 mL.

7.9 Add 1 mL of $K_2S_2O_8$ solution and 1 mL of ferric nitrate solution, and heat in a water bath of 60°C for 10 min.

$K_2S_2O_8$ oxidizes Tc to +7; if the Tc is not oxidized, it will be coprecipitated subsequently with $Fe(OH)_3$.

7.10 Add saturated NaOH solution until the sample solution is basic to pH paper.

7.11 Dilute the solution to 40 mL with water, and mix thoroughly with a glass stirring rod.

7.12 Centrifuge for 2 min.

7.13 Pipet 2 mL of the supernate into a liquid-scintillation counting vial, add 15 mL of liquid-scintillation mix, and mix thoroughly.

7.14 Pipet the ^{99}Tc standard solution into the vial, shake, and count for 1 min.

7.15 Count 15 mL of liquid-scintillation mix, and calculate the background in counts per min.

8.0 CALCULATIONS

8.1 Technetium-99 concentrations in sediment and soil will be calculated using the following equation.

$$^{99}\text{Tc, pCi/g of sample} = \frac{A}{B-C} \cdot \frac{C \cdot D}{E \cdot F}$$

where:

A = Activity of ^{99}Tc standard addition (dpm)

B = Count rate of ^{99}Tc standard addition plus sample aliquot, corrected for background (cpm)

C = Count rate of sample aliquot corrected for background (cpm)

D = Dilution factor; e.g., (40/2) (200/20) = 200

E = Conversion factor = 2.22 dpm/pCi

F = Weight of sample (g).

9.0 PRECISION AND ACCURACY

9.1 Analyses of known samples have indicated a limit of error, at the 95 percent confidence level, of 200 pCi/g at the 1250-pCi/g level. This approximates 8 percent relative standard deviation.

9.2 A positive bias of 100 pCi/g (8 percent relative) has been determined at the 1250-pCi/g level.

10.0 REFERENCE

1. Anders, Edward, November, 1960. The Radiochemistry of Technetium; NAS-NS-3021, National Academy of Sciences.

DETERMINATION OF TECHNETIUM-99 IN AIR FILTERS
(Method EC-260)

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the measurement of technetium-99 (^{99}TC) collected on air filters.

1.2 The lowest concentration of activity reported is 300 pCi per filter.

2.0 SUMMARY OF METHOD

2.1 Technetium-99 is collected with particulate materials on an air filter, and is leached from the filter with nitric acid.

2.2 Persulfate is added to ensure oxidation of Tc to +7, and iron is added as a coprecipitant of impurities; e.g., uranium and its daughters.

2.3 The solution is made basic and centrifuged. An aliquot of the supernate is mixed with a liquid scintillator and the ^{99}Tc is counted on a liquid-scintillation beta spectrometer.

2.4 A known amount of ^{99}Tc is added, the mixture is counted again to determine counting efficiency, and the activity of ^{99}Tc on the air filter is calculated.

3.0 INTERFERENCES

3.1 Interferences include beta-emitting nuclides that are soluble in a basic solution, such as ^{90}Sr. Interference by high-energy beta emitters, such as ^{40}K, is minimized by appropriate energy-window selection on the spectrometer.

4.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

4.1 Air-filter samples are protected in plastic envelopes while awaiting analysis.

5.0 APPARATUS AND EQUIPMENT

5.1 Liquid-scintillation beta spectrometer.

5.2 Liquid-scintillation counting vials - Plastic or glass, 20 mL volume.

5.3 Centrifuge - For 50-mL tubes.

5.4 Centrifuge tubes - Plastic, 50 mL, scribed at the 40 mL level.

5.5 Filter paper - Whatman No. 41.

5.6 Pipets - 50 mL.

6.0 REAGENTS

6.1 Liquid-scintillation mix - Insta Gel, Packard Instrument Co.

6.2 Potassium persulfate solution (5 percent W/V) - Dissolve 50 g of $K_2S_2O_8$ in water and dilute to 1 L.

6.3 4 M HNO_3 - Dilute 250 mL of concentrated HNO_3 to 1 L.

6.4 Ferric nitrate solution (10 percent w/v) - Dissolve 100 g of $Fe(NO_3)_3 \cdot 9H_2O$ in water and dilute to 1 L.

6.5 ^{99}Tc standard solution - 200,000 dpm/mL, prepared by appropriate dilution of standard solution available from Amersham/Searle.

6.6 Sodium hydroxide, saturated - Dissolve 347 g NaOH in 100 mL of H_2O.

7.0 PROCEDURE

7.1 Place the air-filter sample in a 100-mL glass beaker and add 40 mL of 4 M HNO_3.

7.2 Heat at 60 to 80°C for 1 h to leach the Tc from the filter.

7.3 Filter the leaching solution through a Whatman No. 1 filter paper, and dilute the filtrate to 50-mL in a volumetric flask.

7.4 Pipet 10 mL of the solution into a 50-mL plastic centrifuge tube scribed for 40 mL.

7.5 Add 2 mL of potassium persulfate solution and heat in a water bath (60 to 80°C) for 10 min to ensure oxidation of Tc to +7. If the Tc is not oxidized to +7, it will be coprecipitated with $Fe(OH)_3$.

7.6 Add 1 mL of ferric nitrate solution and stir with a glass rod.

7.7 Add saturated NaOH until solution is basic to pH paper.

7.8 Dilute the solution to 40 mL with water, and mix thoroughly.

7.9 Centrifuge for 2 min.

7.10 Pipet 2 mL of the supernate into a liquid-scintillation counting vial, add 15 mL of liquid-scintillation mix, and mix thoroughly.

7.11 Count the ^{99}Tc for 20 min in a liquid-scintillation beta spectrometer.

7.12 Pipet 50 mL of ^{99}Tc standard solution into the vial, shake, and count for 1 min.

7.13 Count 15 mL of liquid-scintillation mix, and calculate the background in counts per minute.

8.0 CALCULATIONS

8.1 Technetium-99 concentrations in air filters will be calculated using the following equation.

$$^{99}\text{Tc on air filter, pCi} = \frac{A}{B-C} \cdot \frac{C \cdot D}{E}$$

where:

A = Activity of ^{99}Tc standard addition (dpm)

B = Count rate of ^{99}Tc standard addition plus sample aliquot correct for background, cpm

C = Count rate of sample aliquot corrected for background (cpm)

D = Dilution factor; e.g., (40/2) (50/10) = 100

E = Conversion factor = 2.22 dpm/pCi.

9.0 PRECISION AND ACCURACY

9.1 The relative standard deviation of this method is 10 percent at the 10,000 pCi level.

9.2 Analyses of standard filters did not indicate the presence of a significant bias.

10.0 REFERENCE

1. Anders, Edward, November, 1960. The Radiochemistry of Technetium; NAS-NS-3021, National Academy of Sciences.

AMERICIUM-241 AND CURIUM-244 IN WATER, RADIOCHEMICAL METHOD
(Method EC-102)

1.0 SCOPE AND APPLICATION

1.1 This method is applicable for the measurement of americium and curium in potable and industrial waters.

1.2 The lowest reported concentration of americium-241 and curium-144 in water is 3×10^{-3} pCi/mL (0.0066 dpm/mL) when using a 100-mL aliquot.

2.0 SUMMARY OF METHOD

2.1 Americium-243 tracer is equilibrated with the sample activities of americium and curium; subsequently all of these isotopes are coprecipitated with calcium as the fluorides.

2.2 The isotopes are then extracted into a quaternary amine, stripped with HNO_3, and extracted into thenoyltrifluoroacetone-xylene.

2.3 The final extract is dried on a stainless steel disc and evaluated by alpha spectrometry, using the ^{243}Am tracer as the basis for calibration of each, the ^{241}Am and the ^{244}Cm concentration.

3.0 INTERFERENCES

3.1 Radioactive interferences normally present are removed by the purification steps which are part of this procedure. The final measurement, by alpha pulse-height analysis, will indicate whether interferences are present.

3.2 There is evidence that curium does not follow the chemical separations in this procedure as quantitatively as americium, and further studies are being considered to evaluate this question.

Americium-241 recoveries are normally 75 percent ±10 percent, compensated by the use of ^{243}Am tracer; the same recovery factor is applied to the curium-244 measurement.

4.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

4.1 Collect the samples in new glass bottles, if possible. Use of plastic containers is permissible if it is known that no contaminants are present in the containers.

4.2 Samples may be preserved with nitric acid by adding 2 mL of concentrated HNO_3 per liter of sample.

5.0 APPARATUS AND EQUIPMENT

5.1 pH meter with combination electrode.

5.2 Hot plate.

5.3 Extraction vial - 50 mL with plastic-lined screw cap.

5.4 Wrist-action shaker.

5.5 Centrifuge - With head to accommodate 50-mL vials.

5.6 Vortex mixer.

5.7 Stainless steel alpha counting discs.

5.8 Fisher burner.

5.9 Alpha pulse-height analyzer - Minimum 200 channels.

6.0 REAGENTS

6.1 ^{243}Am tracer solution (10 dpm/mL) - Standardize an available ^{243}Am solution and prepare a 10 dpm/mL solution in 2 M HNO_3. Alternatively use NBS SRM 4332 or 4333.

6.2 Calcium nitrate solution (50 mg Ca/mL) - Dissolve 11.8 g of $Ca(NO_3)_2 \cdot 4H_2O$ in water and dilute to 100 mL.

6.3 Sodium fluoride solution (saturated) - Place 10 g of NaF in a polyethylene bottle. Add 100 mL of water, shake well, and let stand until the solution is saturated.

6.4 Aluminum nitrate solution - Acid-deficient. Dissolve 1050 g of $Al(NO_3)_3 \cdot 9H_2O$ in a minimum of H_2O by heating. Add 100 mL of concentrated NH_4OH slowly and stir until all of the precipitate dissolves. Dilute to 1 L with water.

6.5 Adogen 464 (Amine) solution (30 percent w/v) - Dissolve 30 g of Adogen 464 (or equivalent) in 100 mL of xylene. Equilibrate twice with fresh 50 mL portions of the $Al(NO_3)_3$ solution (Section 6.4).

6.6 Ammonium nitrate solution (saturated) - Place 80 g of NH_4NO_3 in a polyethylene bottle. Add 100 mL of H_2O, shake well, and let stand until the solution is saturated.

6.7 Nitric acid - Concentrated.

6.8 Nitric acid (8 M) - Slowly add 500 mL of concentrated HNO_3 to 400 mL of H_2O. Mix well and dilute to 1 L.

6.9 Nitric acid (0.1 M) - Add 6.25 mL of concentrated HNO_3 to 200 mL of H_2O and dilute to 1 L.

6.10 Hydrogen peroxide - 30 percent H_2O_2, w/w.

6.11 Hydrochloric acid - Concentrated.

6.12 Methyl orange indicator (0.1 percent) - Dissolve 0.1 g of methyl orange in water and dilute to 100 mL.

6.13 Sodium hydroxide solution (6 M) - Calibrate a polyethylene bottle at the 100-mL mark. Add 24 g of NaOH to the bottle, add 75 mL of water and shake well. Dilute to 100 mL.

6.14 TTA-xylene solution (0.5 M TTA) - Dissolve 55.5 g of TTA (thenoyltrifluoracetone) in xylene and dilute to 500 mL with xylene.

7.0 PROCEDURE

7.1 Pipet an aliquot of the sample water containing 10-50 dpm of ^{241}Am (not exceeding 100 mL) into an appropriately sized beaker. Add a known amount of ^{243}Am tracer (about 10 dpm) and adjust the pH to 1.0. Add 400 uL of calcium nitrate solution, unless the sample is known to contain about 20 mg of calcium, or more.

7.2 Place the beaker on a hot plate and heat to near boiling. Allow to cool to room temperature and adjust the pH to between 1 and 2 with NaOH.

7.3 Add saturated NaF slowly until the sample just begins to be cloudy. Continue to stir occasionally. Allow the precipitate to settle (overnight settling time is better for samples of 200 mL or larger).

7.4 Decant the supernate. Collect the precipitate by centrifugation in a 50-mL vial; remove as much liquid as reasonable without disturbing the precipitate.

7.5 Dissolve the precipitate in a minimum of acid-deficient $Al(NO_3)_3$ solution. Usually 10 mL is sufficient.

7.6 Add an equal volume of the amine solution and extract on the wrist-action shaker for 10 min.

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7.7 Centrifuge for about 2 min to separate the phases. Transfer the organic phase to a new extraction vial.

7.8 Retain the aqueous phase. Repeat Sections 7.6 and 7.7.

7.9 Combine the organic phases and add an equal volume of saturated NH_4NO_3. Mix for 10 min using the vortex mixer.

7.10 Centrifuge and discard the aqueous phase.

7.11 Add about 1/2 volume of 8 M HNO_3 to the organic phase. Mix for 10 min, centrifuge, and transfer the aqueous phase to a 150-mL beaker.

7.12 Repeat Section 7.11 and add the aqueous phase to the 150-mL beaker.

7.13 Place the beaker on a hot plate and evaporate to dryness, adding a few drops of 30 percent hydrogen peroxide just before dryness.

7.14 Add 2 to 3 mL of concentrated HCl and take to dryness. Repeat.

7.15 Flame the beaker to reveal any salts.

7.16 Add a few drops of concentrated HNO_3 and 30 percent H_2O_2 to the residue and heat to dissolve.

7.17 Transfer to an extraction vial with 5 ml of 0.1 M HNO_3, add 3 drops of methyl orange indicator, and adjust the pH to 4 (yellow end point) with 6 M NaOH.

7.18 Add 1 mL of 0.5 M TTA-xylene to the vial, mix on a vortex mixer for 10 min, centrifuge, and transfer (in small increments) all of the TTA-xylene to a stainless steel disc on a hot plate set at 150°C.

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7.19 Repeat Section 7.18, adding the solution to the same disc.

7.20 Flame the disc to a red heat.

7.21 Count the disc using an alpha pulse-height analyzer.

8.0 CALCULATIONS

8.1 Concentrations of Americium-241 and curium-244 in water will be calculated by using the following equations.

$$^{241}\text{Am, dpm/mL} = \frac{A \cdot B}{C \cdot V}$$

$$^{241}\text{Am, pCi/mL} = \frac{A \cdot B}{C \cdot V \cdot E}$$

$$^{244}\text{Cm, dpm/mL} = \frac{D \cdot B}{C \cdot V}$$

$$^{244}\text{Cm, pCi/mL} = \frac{D \cdot B}{C \cdot V \cdot E} .$$

where:

A = Integrated counts of ^{241}Am from pulse analysis

B = ^{243}Am added (dpm)

C = Integrated counts of ^{243}Am from pulse analysis

D = Integrated counts of ^{244}Cm from pulse analysis

V = Aliquot volume (mL)

E = Conversion factor: 2.22 dpm/pCi.

9.0 PRECISION AND ACCURACY

9.1 No definitive statistical data are available, but it is estimated that the precision of this method is 20 percent (RSD) and the accuracy is 20 percent relative.

10.0 REFERENCES

1. Moore, F. L., 1966. "Improved Extraction Method for Isolation of Trivalent Actinide-Lanthanide Elements, from Nitrate Solutions," *Analytical Chemistry*, 38, p. 510.

2. Moore, F. L., December 15, 1960. *Liquid-Liquid Extraction with High-Molecular-Weight Amines*, NAS-NS-3101.

3. Penneman, R. A. and T. K. Keenan, January, 1960. *The Radiochemistry of Americium and Curium*, NAS-NS-3006,.

GAMMA-RAY EMITTING NUCLIDES IN WATER

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the identification and measurement of gamma-emitting nuclides in potable, industrial, and natural waters.

1.2 The minimum detection limits for radionuclides vary depending on gamma-ray branching ratios, counting geometry, photon-detection efficiency, and counting time. For ^{137}Cs and ^{60}Co, the lowest concentration reported (LCR) can be as low as 2.5 pCi/L for a 900-mL sample contained in a Marinelli beaker and counted 16 h on a Ge(Li) detector with a 20 percent efficiency.

2.0 SUMMARY OF THE METHOD

2.1 The sample (of known volume) contained in a polyethylene Marinelli beaker or wide-mouthed jar is counted for a period of time sufficient to yield the desired sensitivity on a high-efficiency Ge(Li) detector and pulse-height analysis system.

2.2 The spectral data are recorded on magnetic tape or other output device and processed by any of several accepted gamma-ray, data-reduction methods (such as the MONSTR Program) to identify and quantify the radionuclides present in the sample.

3.0 INTERFERENCES

3.1 The high resolution afforded by the Ge(Li) spectrometer system minimizes interference among the radionuclides normally encountered.

3.2 When overlapping photopeaks exist, accepted computer routines can be applied to supply the information required for resolution; or, in rare cases, chemical separations may be required.

4.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

4.1 If samples are to be filtered to separate the particulate matter, the filtration should be performed as soon as practicable after sampling. After the sample has been filtered, the filtrate is adjusted to pH 1 (pH paper) with HCl.

4.2 If total activities are to be determined and no filtration is necessary, the sample is adjusted to pH 1 (pH paper) with HCl.

4.3 The sample is either transferred to counting containers or stored in glass or plastic containers.

5.0 APPARATUS AND EQUIPMENT

5.1 Polyethylene Marinelli beakers - 1-L capacity.

5.2 Polypropylene jars - 8-cm diameter by 8-cm depth.

5.3 Ge(Li) detector(s) - 20 percent relative efficiency recommended.

5.4 Multichannel pulse-height analyzer - 4096 channels or better.

5.5 Magnetic tape storage device, or equivalent.

5.6 Micropipet - Calibrated.

6.0 REAGENTS

6.1 Mixed-radionuclide solution, standardized solution of mixed, gamma-ray-emitting radionuclides. Suitable standards are available on a non-periodic basis from NBS and several commercial suppliers.

6.2 Hydrochloric acid - Concentrated HCl.

7.0 PROCEDURE

7.1 Standardization

7.1.1 Using a micropipet, transfer an aliquot of standardized, mixed-radionuclide solution to a Marinelli beaker or a jar. The activity of the aliquot should be suitable to the analytical range of interest.

7.1.2 Add distilled water and HCl to bring to the required volume and maintain a 1 N acid concentration. Cap the container, seal with plastic tape, and mix well.

7.1.3 Place the container in a plastic bag to protect against contamination. Position on the Ge(Li) detector and accumulate a spectrum such that the photopeaks of the standard emissions have a net count approaching 10,000.

7.1.4 Transfer the spectrum to magnetic tape. Process these data to determine the net count rate, R, of each of the standard photopeaks.

7.1.5 Correct the information on the standard certificate for radioactive decay; and, with reference to the aliquot used, determine the photon emission rate, A, for each nuclide at the time of measurement.

7.1.6 Compute the counting efficiency, E, at each energy using the following formula.

$$E = R/A$$

7.1.7 Using these data, make a plot of counting efficiency, ε, as a function of gamma energy, E, on logarithmic paper. Draw a continuous curve through the plotted points to provide a graph useful for determining counting efficiency at any energy within the range of the calibration.

7.2 Place the sample container, Marinelli beaker or jar, in its plastic bag on the Ge(Li) detector and accumulate a spectrum over a period sufficient to provide desired sensitivity.

7.3 Transfer the spectrum to magnetic tape. Process these data to determine the energy and net count rate, R, of each photopeak in the spectrum.

7.4 With reference to gamma-ray energy graphs, Section 7.1.7, identify the radionuclides present in the sample.

8.0 CALCULATIONS

Compute the activity concentration of each radionuclide using the following formula.

$$\text{pCi/L} = \frac{R \times C}{(I)(L)\varepsilon}$$

where:

R = Net count rate in photopeak (cps)

ε = Counting efficiency at E (from Section 7.1.7) (cps/dps)

I = Absolute intensity (abundance fraction) of emission at E

L = Volume of sample

C = Conversion factor: 27 pCi/dps.

9.0 PRECISION AND ACCURACY

9.1 Precision is a function of activity and counting time and can be as low as 1 percent.

9.2 Accuracy is limited to ±6 percent due to uncertainty in detector calibration.

10.0 REFERENCES

1. A Handbook of Radioactivity Measurements Procedures, NCRP Report No. 58, Nov. 1978.

2. Radiochemical Analytical Procedures for Analysis of Environmental Samples, EMSL-LV-0539-17, March 1979.

3. Radioactive Decay Gamma Ray Spectra Compilation, DLC-19, Union Carbide Corporation, Nuclear Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

4. Emery, J. F. and F. F. Dyer, July 29-31, 1974. MONSTR: Multi-Element Determination in Environmental Neutron Activation Analysis Using MONSTR, Proceedings of 2nd International Nuclear Methods in Environmental Research Conference, University of Missouri, Columbia, Missouri.